Heavy Metal Contamination in Water and Sediment of To Lich River in Inner City Hanoi(Dissertation_全文)

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TABLE OF CONTENTS

CHAPTER 1. GENERAL INTRODUCTION

1.1. GENERAL CHARACTERISTICS OF HANOI CITY

Hanoi is capital city of Vietnam, located in Red river delta at 21°01′42″N and 105°51′12″E (Fig. 1.1). The city features a tropical monsoon climate with two distinct seasons: Winter dry season (November to April) and summer rainy season (May to October), which contains nearly 85% of total precipitation. The annual precipitation is much changing year by year from 1200 to 2300 mm (Fig. 1.2). In rainy season especially in July and August, there are some cases with rainfall up to 150 mm/day when storms come. In contrast, dry season averages only 12 mm in December and January.

Hanoi was expanded in 2008 and currently covers a total area of 3,329 km^2 with a population of 6.7 million people in 2011. The inner Hanoi capital comprised ten districts, namely Ba Dinh, Hoan Kiem, Dong Da, Hai Ba Trung, Tay Ho, Thanh Xuan, Cau Giay, Hoang Mai, Ha Dong and Long Bien. In the past ten years, population in Hanoi increased 120,000 people annually, including many from in-migration. Average population density is 2,013 people/km^2, however in some inner districts like Dong Da and Hai Ba Trung, the figure reached up more than 35,000 people/km^2. Currently, population in inner city is 2.6 million people with annual growth rate of 3.8%, of which in-migration contributes roughly 3%.

There are several rivers running through Hanoi region, namely Hong, Duong, Nhue rivers, and To Lich River (TLR) system (Fig. 1.1). Among them, Nhue and TLR system are responsible for receiving and conveying wastewaters for inner city Hanoi. TLR system includes four main rivers with a total length of 38.9 km and covers a basin area of 77.5 km^2. (1) TLR covers a basin of 20 km^2 and has a length of 17 km, a width of 20 - 45 m, and a depth of 2 - 4 m, starting from West lake in the North, receiving wastewaters from western Hanoi then discharging to Nhue River in the South with maximum flow of 30 m^3/s. (2) Kim Nguu River originates from central Hanoi and joins with TLR at Thanh Liet. The river has a length of 11.9 km, a width of 25 - 30 m, and a depth of 2 - 4 m, covering a basin area of 17.3 km^2. Kim Nguu was embanked in 2002 and resulted in a maximum flow of 15 m^3/s. (3) Set River starts from central south Hanoi with a length of 6.8 km, a width of 3 - 4 m, and a depth 1.5 - 2.5 m, covering an area of 7.1 km^2. The river has maximum flow of 8 m^3/s. Water from Set River is discharged to upstream of Kim Nguu River. (4) Lu River also starts from central south of Hanoi with a length of 6,7 km, a width of 7 - 10 m, and a depth of 2 - 3 m, covering a basin of 10.2 km^2. The river has a maximum flow of 6 m^3/s. Lu River discharges water to TLR at downstream before confluence of Kim Nguu with TLR. Besides, there are approximately 25 small channels with a width of 3 - 5 m, a depth of 1.5 - 2.5 m, and a total length of 18.1 km in inner Hanoi city. In addition, Hanoi is known as "city of lakes" with a total of 518 large and small ones (Fig. 1.1). Besides serving as recreations, these lakes also function as receiving untreated wastewaters in inner Hanoi city leading to many environmental problems.

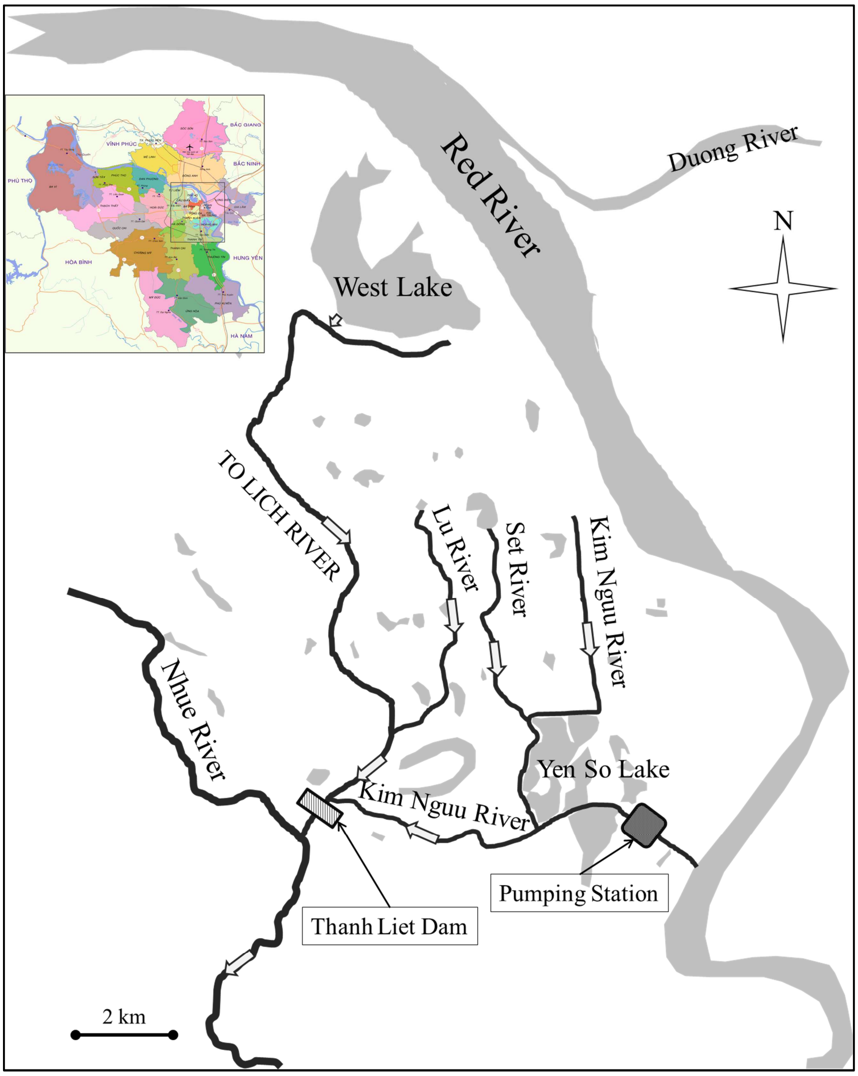

Fig. 1.1 River system and lakes in Hanoi

To Lich River system is under high polluted condition as result of diversity of wastewaters discharged from various sources such as industry, hospitals, households, agriculture, etc. There are about 2 million permanent citizens living in inner city Hanoi (GSO 2010) and seasonal citizens, generating domestic wastewater to TLR system an estimated volume of more than 190,000 m^3/day. Meanwhile, discharge from industries ranges between 240,000 to 263,000 m^3/day, occupying 53 - 58% of the total wastewater from inner city. There are five industrial zones located in Hanoi including 99 large manufacturing plants of all types of industries, which release wastewater to TLR system (Table 1.1). In addition with 369 large and medium scale industries, there are 14,000 small industry and handicrafts located in Hanoi (HENRD 2002). Twenty nine hospitals and many big health centers with more than 25,000 beds also discharge roughly 6,000 m^3 wastewater per day to TLR system (HENDR 2009).

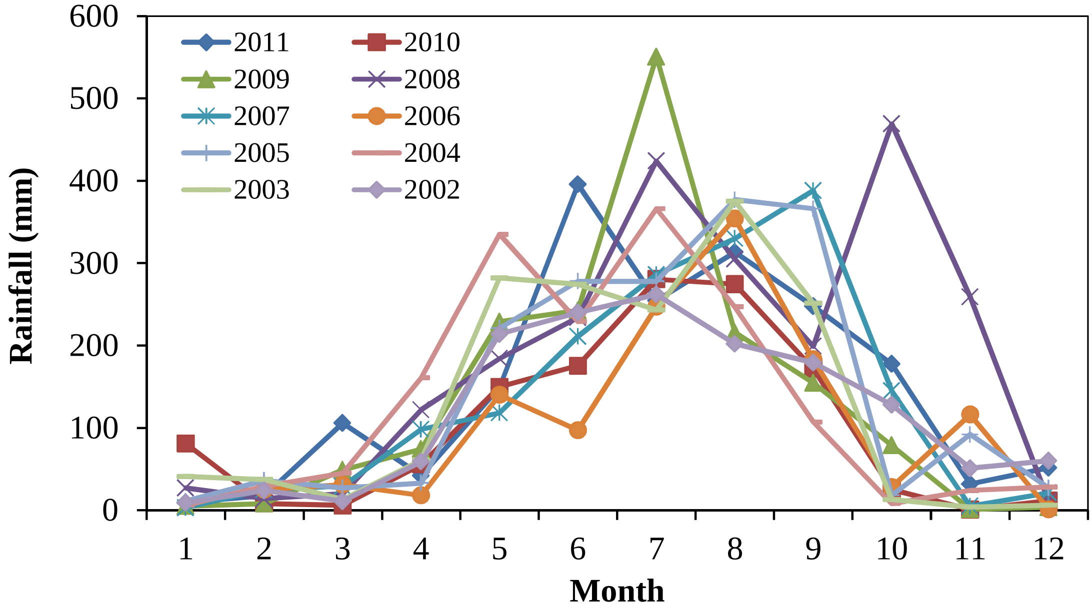

Figure 1.2 Average monthly rainfall during 2002-2011

To improve water flow rate and reduce stagnation, the embankment was carried out in many reaches of all four rivers in TLR system. In addition, to reduce pollution impacts from TLR system, which may lead to deteriorate water supply source for downstream provinces of Nhue River, regulatory Thanh Liet Dam (TLD) was built nearly at the end of TLR and Yen So pumping station was built in southeastern Hanoi (Fig. 1.1). Recently, TLR system functions as: (1) TLD is open when water level in Nhue River is low, then water from TLR drains naturally to Nhue River; (2) TLD is closed when water in Nhue River runs higher than in TLR and/or TLR water is too polluted, which may affect water quality of Nhue River. In case of closing dam, water from TLR flows into Yen So regulating reservoir and is finally pumped to the Red river (Fig. 1). In fact, to reduce pumping costs, even highly polluted water is still discharged to Nhue River leading to degradation of water quality at the downstream. In general, Thanh Liet Dam is opened more than 320 days annually.

Table 1.1. List of manufacturing plants of five industrial zones in basin of To Lich River system, Hanoi

Type of industry	**Thuong Dinh - Nguyen Trai**	**Minh Khai - Vinh Tuy**	**Truong Dinh - Duoi Ca**	**Van Dien - Phap Van**	**Cau Buou**
Mechanical	14	13	3	8	3
Construction material	-	6	-	2	1
Food processing	1	3	6	-	-
Textile	4	11	2	-	-
Leather	3	1	-	-	-
Printing	-	1	-	-	-
Paper	1	-	-	-	-
Ceramic	2	-	1	-	-
Chemical	2	-	-	2	1
Others	3	3	1	1	-
Total	30	38	13	13	5

1.2. Wastewater and sediment characteristics and their impacts on environment, human, and ecosystem

The world is facing with problems related to the management of wastewaters. This is due to industrialization, population increase, and urbanized societies (USEPA 1993; McCasland et al. 2008). The wastewaters generated from domestic and industrial activities constitute major sources of water pollution load. This is a great burden in terms of wastewater management and can consequently lead to a point-source pollution problem, which not only increases treatment cost considerably, but also introduces a wide range of chemical pollutants and microbial contaminants to water bodies (USEPA 1993, 1996; Eikelboom and Draaijer 1999; Amir et al. 2004).

The level of treatment ranges from no treatment to very sophisticated and thorough treatments. Wastewaters are discharged to a wide variety of receiving environments: lakes, ponds, streams, rivers, estuaries, and oceans. Wastewaters do contain pollutants of concern since even advanced treatment systems are unable to remove all pollutants and chemicals. Several environmental and health impacts resulted from insufficient wastewater treatment have been identified in the scientific literature (Musmeci et al 2009; Saracci and Vineis 2007; Pruss-Ustun and Corvalan 2007, 2006; Rothman and Greenland 1998; Suser 1991; and many others) and actions need to be taken to reduce these impacts.

The impacts, that wastewaters may have on water quality, plant and animal life, human health, and beneficial water uses, include:

- decaying organic matter and debris can use up the dissolved oxygen in water bodies, affecting life of aquatic biota;

- excessive nutrients, such as phosphorus and nitrogen, can cause receiving waters over-fertilization, which can be toxic to aquatic organisms, reduce availability of oxygen, alter habitat, and lead to a decline in species and/or population;

- chlorine compounds and inorganic chloramines can be toxic to aquatic invertebrates, algae, etc.;

- bacteria, viruses, and disease-causing pathogens can pollute playground near water bodies, leading to human waterborne diseases and restrictions on recreation;

- heavy metals, such as mercury, lead, cadmium, chromium, arsenic, etc., can have acute and chronic toxic effects on species.

The process of collection and treatment of wastewaters also results in the release of certain volatile chemicals into the air. The chemicals typically released in the large volume include; methane, carbon dioxide, oxides of nitrogen and hydrogen sulfide, and various other chemicals can be released to a smaller extent.

The physic-chemical characteristics of wastewaters of special concern are pH, dissolved oxygen, oxygen demand (chemical and biological), solids (suspended and dissolved), nitrogen (nitrite, nitrate and ammonia), phosphate, and heavy metals (DeCicco 1979; Larsdotter 2006).

The pH is an important quality parameter of wastewaters. It is used to describe the acid or base properties of wastewaters. pH values less than 5 and greater than 10 indicate the presence of industrial wastewater and are non-compatible with biological operations. The pH range of 6 - 9 is usually in the existence of biological life (USEPA 1996; Gray 2002). Dissolved oxygen (DO) is another parameter in water requiring for the respiration of aerobic microorganisms as well as all other aerobic life forms. The actual quantity of DO is governed by the solubility, temperature, partial pressure of the atmosphere, and the concentration of impurities such as salinity and suspended solids in the water (USEPA 1996; Metcalf and Eddy 2003). While, oxygen demand in the form of BOD or COD is the amount of oxygen used by microorganisms as they feed upon the organic solids in wastewaters (Water Environmental Federation 1996; Gray 2002; FAO 2007). In which, the 5-day BOD is the most widely organic pollution parameter applied to wastewaters. Wastewaters normally comprise 99.9% water and 0.1% of solids, in which discharges from industrial and domestic sources respond high portion of those solids.

Phosphorus in water is essential constituents of living organisms. However, when phosphorus input to water is higher than natural-balanced condition (Rybicki 1997), it may lead to extensive algal growth (eutrophication). Controlling phosphorus discharge from domestic and industrial wastewaters is a key factor in preventing eutrophication in surface waters (Department of Natural Science 2006). Phosphate itself does not have notable adverse effects on human health. On the other hand, nitrogen is important in wastewater management and can have adverse effects on ecology and human, if concentration is higher than 10 mg/L. Despite the fact that nitrates in some levels affect infants, but do not pose any direct threat to older children and adults, it indicates the presence of other serious residential or agricultural contaminants, such as bacteria and pesticides (McCasland et al. 2008). Methemoglobinemia is the most significant health problem associated with nitrate in water. Similarly, nitrogen in the form of ammonia is toxic to fish and exerts an oxygen demand on receiving water by nitrifiers (CDC 2002).

Metals are of importance in water. The metals of importance in wastewater treatment are As, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Na, V, and Zn. Living organisms require varying amounts of some metals (Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, and Zn) as nutrients for their proper growth. While, other metals (Ag, Al, Cd, Au, Pb, As, and Hg) have no biological role and hence are non-essential (Metcalf and Eddy 2003; Hussein et al. 2005). Heavy metals are one of the most persistent pollutants in wastewaters. Unlike organic pollutants, they cannot be degraded, but accumulate throughout the food chain, producing potential risks on human health and ecological disturbances. Their over-presence in wastewaters is due to discharges from domestic, industrial, vehicle emission, etc. The accumulation of heavy metals in wastewaters depends on many local factors, such as the type of industries, way of life, and awareness of their impacts on the environment through the careless disposal of wastes (Hussein et al. 2005; Silvia et al. 2006). The danger of heavy metal pollutants in wastewaters lies in two aspects. First, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological food chain (Fuggle 1983). Although heavy metals are present in small quantities in natural, it is almost exclusively through human activities that these levels are increased to toxic levels in wastewaters (Nelson and Campbell 1991). Human can be exposed to chemicals in wastewaters in various ways. They may ingest small amounts of pollutants from consuming crops which are irrigated by wastewaters, aquaculture products which live in polluted water body, and from absorbing contaminants through their skin while contacting with wastewaters.

The major microorganisms found in wastewaters are viruses, bacteria, fungi, protozoa, and helminthes. Although those microorganisms are criticized as a main source in contributing to numerous waterborne diseases to human, they play many beneficial roles in wastewater treatment as removing dissolved organic matter (Kris 2007), using in fixed film systems, suspended film systems or lagoon systems in treatment plant to enhance degradation of solids for less sludge production (Ward-Paige et al. 2005a). In addition, wastewater microbes are also involved in nutrient recycling, such as phosphate, nitrogen, and heavy metals. If nutrients that are trapped in dead materials are not broken down by microbes, they will never become available to help sustain the life of other organisms. Microorganisms are also responsible for the detoxification of acid mine drainage and other toxins in wastewaters (Ward-Paige et al. 2005b).

The investigation of sediments from the water bodies is of great interest in aquatic systems, since sediment quality is a good indicator of pollution in water column, where it tends to accumulate the heavy metals and other organic pollutants, as well as provide information on the impact of pollution sources. The potential environmental damage of water bodies might be comparatively small if heavy metals are ultimately fixed in sediments (Zoumis et al. 2001). Metal composition in the sediment may be controlled by natural (e.g., mineralogy, weathering) and anthropogenic processes (Nesbitt 1979). The chemical composition of the sediments can be used as a powerful tool to determine their sources (Vital and Stattegger 2000). While, horizontal distribution of metals has provided evidence that lateral variations in the chemical composition of surface sediments act as a guide to local pollution centers (Förstner 1981).

A critical factor for sediment toxicity is contaminant bioavailability, the degree to which contaminants can be taken up by plants and animals (Ankley et al. 1996). Sediment parameters that affect heavy metal bioavailability include cation exchange capacity, total organic carbon, Fe and Mn oxides, as well as the relationship between acid volatile sulfides and simultaneously extracted metals.

Cation exchange capacity is based on the surface area of sediment grain particles available for binding cations, such as hydrogen (H+) and free metal ions (e.g., Mn+2). Sediments with a high percentage of small grains, such as silt and clay, have high surface-to-volume ratios and can absorb more heavy metals than sediments composed of larger grains. Total organic carbon is added to sediments primarily through the decomposition of plant and animal matter, and domestic and industrial discharges. Organic carbon can directly adsorb heavy metals from solutions applied to sediments (Liber et al. 1996). However, it can also contain heavy metals accumulated by plants which is discharged and decomposed in sediment (Peltier et al. 2003). Nonetheless, high percentages of small grains in sediment are generally associated with reduced heavy metal bioavailability and toxicity (Ankley et al. 1996).

The dominant geochemical processes responsible for the exchange of metals at the water-sediment interface are adsorption and precipitation (Salomons and Forstner 1984; Wang et al. 1997). Fe and Mn oxides and organic matter either as bulk phases or as coatings of mineral particles are the main binders in sediments (Tessier et al. 1980). Binding fractions of heavy metals in the sediments can be divided into five groups: exchangeable, carbonates, hydroxides, organic and residuals. Both Fe and Mn can remove other heavy metals from solution through oxidation, thus making them less bioavailable (Fan and Wang 2001). The ways for doing this is by precipitating heavy metals from solution during oxide formation (Simpson et al. 2000) and is direct adsorption onto preformed oxides (Dong et al. 2000). Sulfide is known to interact with Fe under anaerobic conditions to form a solid, iron sulfide (FeS). Other heavy metals such as Cu, Pb, Ni, Zn can be removed from solution by displacing Fe and binding to the sulfide. This process has led to a relatively new parameter for evaluating sediment toxicity, so called simultaneous extracted metal minus acid volatile sulfide (SEM-AVS). The term AVS represents the amount of sulfide in sediments available for binding heavy metals; SEM represents the amount of heavy metals in sediment that could be available to plants and animals. If SEM exceeds AVS, the sediments are potentially toxic (Di Toro et al. 1990; Hansen et al. 1996).

1.3. Benefits of wastewater reuse in agriculture and its concerned problems

Sewage farm has been developed for more than 100 years in industrialized countries like England, France, Germany and Australia, in which sewage was disposed to the farm for natural treatment (now known as recycle and reuse), supporting water and nutrient in low cost for farm. However, many of those farms were abandoned because of many environmental problems, transmission of diseases, and contaminated products (Shevah 1999).

Municipal wastewater is less expensive and considered an attractive source for irrigation in many countries, especially in arid and semi-arid countries. Advantages of reuse of wastewaters in agriculture include: conserving water, cost-efficient method for domestic wastewater disposal, reducing pollution of water bodies, reducing input costs for artificial fertilizers, increasing crop yields, and providing a reliable water supply. However, it also contains a number of important disadvantages (Bahri and Brissaud 1996; Weber et al. 1996) including: health risks to both irrigators who are in prolonged contact with wastewaters and consumers of crops which are irrigated with wastewaters, contamination of ground water especially with nitrates, buildup heavy metal pollutants in the soil, and creation of habitat for disease vectors.

Since wastewater treatment technology has been improved, resulted in cost-effective agriculture application. The reuse of treated wastewaters is receiving an increasing attention as a reliable water resource. In many countries, treating wastewater for reuse is important of water resources planning and implementation. This is aimed at releasing high quality water supplies for potable use. Some countries, such as Jordan and Saudi Arabia have national policies to reuse treated wastewaters. The general acceptance is using wastewater in agriculture, justifying on agronomic and economic grounds, although care must be taken to minimize adverse impacts on environment and human health (FAO 1992; Metcalf and Eddy 2003; Rietveld et al. 2009; Sowers 2009). The option of reuse of wastewater at least in agriculture is becoming necessary and possible as a result of climate change, which leads to droughts and water scarcity, and the fact that discharge regulations have been becoming stricter, leading to a better wastewater quality (Rietveld et al. 2009).

Management of irrigation with wastewaters should consider the nutrient content in relation to the specific crop requirements and the concentrations of plant nutrients in the soil, and other soil fertility parameters. In many areas of developing countries, untreated wastewaters are used directly to small plots of vegetables and salad crops, which are easily consumed raw as salad. The public health risks coming from this are obvious (Mead and Griffin 1998; WHO 2004). However, such risks can be controlled by treating wastewaters properly before irrigating crops, which minimize the transfer of pathogenic and toxic contaminants into the agricultural products, soils, and surface and groundwater (Batarseh et al. 1989). The nutrient supply from wastewaters to the soil is obvious such as

N, P, as well as organic matters (Sommers 1977; Pomares et al. 1984), but there is a concern about the accumulation of potentially toxic elements such as Cd, Cu, Fe, Mn, Pb, and Zn from both domestic and industrial discharges (Pescod, 1992). Nitrogen is much available in wastewater especially from domestic source and is in forms of usability for crops; organic nitrogen, ammonia, nitrate and nitrite, in which three later make up the inorganic forms (Hurse and Connor 1999). Nitrogen in different forms is required by all organisms for the basic processes of life to make proteins, grow and reproduce. Therefore, wastewaters and its nutrients can provide significant benefits to the farming communities and society in general.

1.4. AIMS OF THIS STUDY

In being urbanized societies like city Hanoi, wastewaters are dynamics in terms of both quality and quantity. There are a number of responsible reasons; population increase especially from in-migration and seasonal citizens, which is out of predictability leading to uncertainty of amount and quality of their wastewaters, construction blooming, and a number of industrial zones which were established in inner city for a long history. In addition, wastewater treatment has not been much taken care, leading to serious environmental problem especially for water bodies such as rivers, lakes and their surrounding recreations. Monitoring and assessing pollution levels and quality of water bodies for both water and sediment, and discriminating pollution sources should be carried out periodically which will serve decision makers in issuing environmental regulations to improve wastewater quality at sources before discharging to common sewage system, and in planning wastewater treatment plant system, which collects all wastewaters and treat them to suitable using purpose such as for irrigation.

The aims of the study are:

To discriminate sources of heavy metals in sediment and water of To Lich River using multivariate statistical approaches.

To assess heavy metal pollution and exchange between water and sediment system in the To Lich River, inner Hanoi City.

To evaluate the recovery of To Lich River after nine years embankment using river quality index, with special reference to heavy metals.

1.5. OUTLINE OF DISSERTATION

CHAPTER 2 discriminates nature, anthropogenic, and/or mix sources of eight heavy studied metals including Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb using hierarchical cluster and principle component analyses. Meanwhile, enrichment factor and geo-accumulation index were used to evaluate enrichment and contamination levels of heavy metals.

CHAPTER 3 assesses contamination levels of nine study sites, which corresponds to its discharge sources as domestics, industrials, and/or mix. Besides using enrichment factor and geo-accumulation index, quality guidelines including a threshold effect concentration, a probable effect concentration (PEC), and mean PEC quotient were also used to evaluate impacts that each site may pose to aquatic organisms. In addition, the current study area was also compared to some polluted rivers around the world to understand the extent of heavy metal pollution in To Lich River.

CHAPTER 4 evaluates current quality of To Lich River compared to that before embankment nine years ago by using relative river quality index, with special reference to quality of water and sediment through their heavy metal concentrations. The chapter also includes estimation of total sediment currently accumulated in river bed and costs required to treat those sediment to environmental friendly condition, estimation of heavy metal and total organic carbon loads in each concerned river reach corresponding to its discharged sources, and total load at the end of To Lich River which is discharged daily to Nhue River in South Hanoi.

CHAPTER 5 presents general discussion and management implications for To Lich River system basin.

CHAPTER 6 summarizes main findings in dissertation.

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CHAPTER 2. SOURCE DISCRIMINATION OF HEAVY METALS IN SEDIMENT AND WATER OF TO LICH RIVER IN HANOI CITY USING MULTIVARIATE STATISTICAL APPROACHES

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ABSTRACT

The concentrations of Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb were determined to evaluate the level of contamination of To Lich River in Hanoi city. All metal concentrations in 0-10 cm water samples, except Mn, were lower than the maximum permitted concentration for irrigation water standard. Meanwhile, concentrations of As, Cd and Zn in 0-30 cm sediments were likely to have adverse effects on agriculture and aquatic life. Sediment pollution assessment was undertaken using Enrichment Factor and Geo-accumulation Index (Igeo). The Igeo results indicated that sediment was not polluted with Cr, Mn, Fe and Ni, and then pollution level increased in order of Cu < Pb < Zn < As < Cd. Meanwhile, significant enrichment was shown for Cd, As, Zn, and Pb. Cluster and principle component analyses suggest that As and Mn in sediment were derived from both lithogenic and anthropogenic sources, while Cu, Pb, Zn, Cr, Cd, and Ni originated from anthropogenic sources such as vehicular fumes for Pb and metallic discharge from industrial sources and fertilizer application for other metals.

Keywords: Geochemical indices, Hanoi, Metals, Multivariate Statistical approaches, Sediment.

2.1. INTRODUCTION

Trace elements, the so-called heavy metals, are one of the serious pollutants in natural environment because of their persistence, toxicity, and bioaccumulation (Fang and Hong 1999; Tam and Wong 2000). Heavy metals tend to be trapped in the aquatic environment and accumulate in sediment, which are probably released to the water through sediment re-suspension, reduction-oxidation reactions, etc. Such processes enhance the dissolved concentration of trace metals in water (Jones and Turki 1997; Wright and Mason 1999). Since sediment acts as the carrier and the potential secondary source of contaminants in river system (Calmano et al. 1990), the degree to which it becomes a source of pollution depends on such factors as the proximity of contaminated sediments, river activity (e.g. water flow rate) and the intensity of geomorphic activity of the river catchment (Martin 2000). Therefore, the analysis of river sediment is a useful method to study the metal pollution in an area.

Heavy metals enter a river from a variety of sources; either natural or anthropogenic (Adaikpoh et al. 2005; Akoto et al. 2008). The concentration of most of the metals in unaffected rivers is very low, which is safe to biotic and is mostly derived from weathering of rock and soil (Reza and Singh 2010). Meanwhile, the main anthropogenic source of heavy metals to affected rivers, especially in inner cities, is from untreated and/or partially treated disposals containing heavy metals from domestic and industrials (Macklin et al. 2006; Nouri et al. 2008; Reza and Singh 2010). It is estimated that there is in between of 30 and 98% of the total metal load accumulated in sediment-associated forms (Gibbs 1973; Salomons and Förstner 1984). Sediment will become a potential non-point source of pollution if it is deposited on the river banks or floodplain (Marcus 1989; Martin 2000).

Hanoi, the capital of Vietnam, has witnessed the rapid economic growth and urban expansion for recent decades, causing severe environmental pollution especially to inner city river system. The domestic and industrial wastewater is untreated or partially treated before discharging to To Lich River, the main drainage river in inner city of Hanoi, resulting in serious deterioration of the water and sediment qualities, and related problems as water-borne diseases. Previous investigations indicated that the concentration of heavy metals in sediment of To Lich River was quite high because of the metallic wastewater discharged from manufacturing plants located in catchment and longtime stagnation (Ho and Egashira 2000; Nguyen et al. 2007; Kikuchi et al. 2009). It is said that heavy metal concentrations in sediment and water in To Lich River exceeded the Vietnamese standard for agriculture (Ho and Egashira 2000; Nguyen et al. 2007), even the contents in water were not exceeding or only for several metals. It was reported that environment in Hanoi city has been improved much in recent years as a result of treatment of industrial wastewater from the enforcement of several environmental regulations. This paper aims to evaluate the current status of heavy metal contamination in 0-10 cm water and 0-30 cm sediment, and to discriminate the possible sources and enrichment of heavy metals in sediment of To Lich River.

2.2. MATERIALS AND METHODS

2.2.1. Study area

The To Lich River has been a significant river throughout history of Hanoi city. The river originates in the West Lake and flows through residential and industrial areas, before joining the Kim Nguu River nearly at downstream, and finally enters Nhue River through Thanh Liet Dam (Fig. 2.1). The dam was constructed to prevent contaminated water of To Lich to Nhue. Its gate is almost closed in dry season and is manually controlled in rainy season according to the water level of To Lich. Total length of To Lich is approximately 17 km, covering a catchment of about 20 km^2. A number of manufacturing plants are located between S3 and S4 (Fig. 2.1), including a complex of factories of mechanical engineering, rubber, soap, and tobacco in Thuong Dinh and Thanh Xuan districts. Meanwhile, leather and paint factories are located near S1 and S6 (Fig. 2.1), respectively. A plastic company is located upstream from confluence with Lu River (Nguyen et al. 2007). The volume of sewage dumped into To Lich was approximately 290 thousand m^3 per day, which accounted two-thirds of wastewater generated from inner Hanoi city (Nguyen et al. 2007).

2.2.2. Sample collection

Surface water and sediment samples were taken from eight sites located along the river (Fig. 2.1) in the dry season, March 2011. Polypropylene bottles were immersed 10 cm deep below the water surface. Then, water samples were acidified with conc. HNO_3 to pH < 2, transported to the laboratory, and stored in a refrigerator until analysis. Sediment samples, on the other hand, were taken at 0-30 cm from the river bed using a self-made sediment sampler and placed in polyethylene bottles.

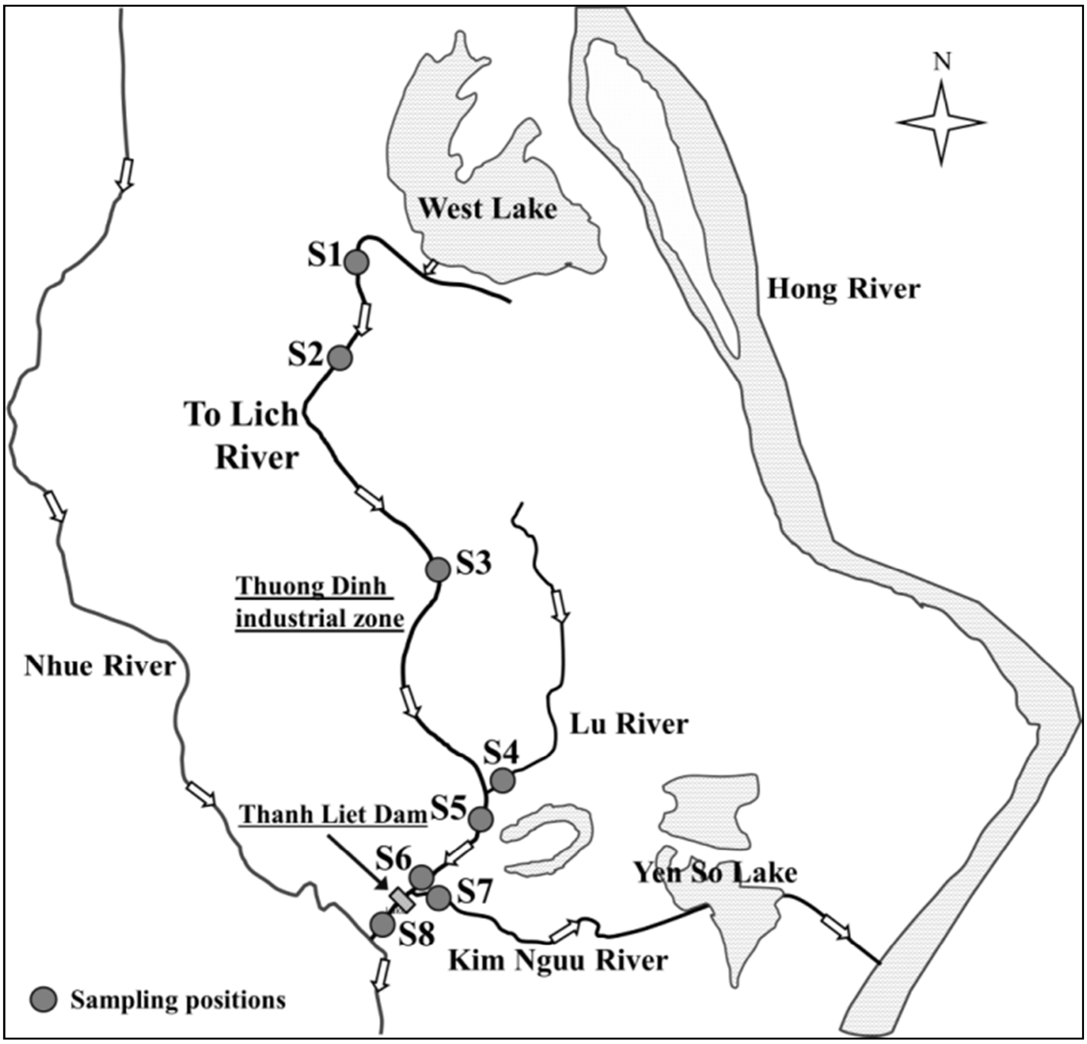


Fig. 2.1 Map of To Lich River catchment showing sampling sites

2.2.3 Chemical analysis

Collected sediments were air-dried and passed through 1-mm stainless steel sieve to remove big particles. The samples were then heated in drying oven at 60^{o}C until constant weight and lightly powdered within an agate mortar for homogenization. A microwave unit was used for the digestion of sediment samples with acid. Briefly, 50 mg dry sediment was placed in a vessel and successively digested with 10 mL of conc. HNO_3 in a microwave digestion system (USEPA 2007). After cooling, the digest was adjusted to 50 mL volume with Mili-Q water and finally filtered through a membrane filter (0.45-μm pore size). Concentration of heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb) in acid-digested sediment and water samples was determined using ICP-MS.

2.2.4. Statistical analysis

Multivariate approaches were used in this study to assess the interrelationships among the measured data, since they have been successfully used in geochemical and ecochemical studies (Soares et al. 1999; Sakan et al. 2009; Li and Zhang 2010).

The Geo-accumulation Index (I_{geo}) introduced by Müller (1981) was employed to assess the heavy metal contamination in sediment by comparing current concentrations with pre-industrial levels. Values of I_{geo} were calculated by the following formula (Eq. 2.1):

$$I_{geo} = \mathrm{Log}_2 \frac{C_n}{1.5B_n} \quad (2.1)$$

where C_n is the concentration of metal *n* examined in the sediment and B_n is the geochemical background concentration of the metal *n*. Factor 1.5 is used because of possible variations in background values due to lithogenic effects. As the background value of the concerned metals in current study site is not available, the earth crust values (Turekian and Wedepohl 1961) were adopted. The values of I_{geo} were classified into seven classes (Müller 1981; Bhuiyan et al. 2010); $I_{geo} \leq 0$ (Class 0: practically uncontaminated), $0 < I_{geo} \leq 1$ (Class 1: uncontaminated to moderately contaminated), $1 < I_{geo} \leq 2$ (Class 2, moderately contaminated), $2 < I_{geo} \leq 3$ (Class 3, moderately to heavily contaminated), $3 < I_{geo} \leq 4$ (Class 4, heavily contaminated), $4 < I_{geo} \leq 5$ (Class 5, heavily to extremely contaminated), $5 > I_{geo}$ (Class 6, extremely contaminated). Class 6 reflects 64-fold enrichment over the background value (Singh et al. 1997).

Enrichment Factor (EF) was used to determine whether metals in sediment were of anthropogenic origin (Simex and Helz 1981). To identify anomalous metal concentration, geochemical normalization of the heavy metal data to a conservative element, such as Al, Fe, and Si was employed. Several authors have successfully used iron to normalize heavy metal contaminant (Schiff and Weisberg 1999; Mucha et al. 2003, Seshan et al. 2010; Varol and Sen 2012). In this study, iron was also selected as a main conservative tracer (while, Mn was also selected for comparison) to discriminate natural from anthropogenic components. The EF of each concerned metal was expressed by the following equation (Eq. 2.2):

$$\mathrm{EF} = \frac{(\mathrm{Metal/Fe})_{\mathrm{sample}}}{(\mathrm{Metal/Fe})_{\mathrm{background}}} \quad (2.2)$$

where $(Metal/Fe)_{sample}$ is the metal to Fe ratio in the sample of interest; $(Metal/Fe)_{background}$ is the natural background value of the metal to Fe ratio. The choice of background values plays an important role in the interpretation of geochemical data, in which several authors (Loska and Wiechula 2003; Olivares-Rieumont et al. 2005; Singh et al. 2005; Pekey 2006b) have successfully used the average shale values or the average crustal abundance data as reference baselines. The background values for EF calculation were similar as those used in the aforementioned Geo-accumulation Index calculation. Value of enrichment factor < 1 indicates no enrichment, 1-3 is minor, 3-5 is moderate, 5-10 is moderately severe, 10-25 is severe, 25-50 is very severe, and > 50 is extremely severe enrichment (Sakan et al. 2009).

Hierarchical clustering analysis is undertaken according to the Ward method (Ward 1963) with Pearson distances (Zhou 2008). Ward method was considered superior in the aspects of giving a larger amount of correct classified observations in comparison with other methods (Sharma 1996). Results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distance between clusters are represented.

Principal component analysis (PCA) has been widely used to identify possible sources of heavy metals in sediments; natural, anthropogenic or mixed (Facchinelli et al. 2001; Micó et al. 2006). PCA reassembles the original variables into several integrated groups unrelated to each other and selects less comprehensive variables from the integrated groups to reflect the original variables according to the actual needs. The result of PCA indicates that heavy metal concentrations can be reduced to several components, which represent all the heavy metals in samples.

2.3. Results and discussion

2.3.1. Heavy metal contamination

The statistical summary for heavy metal values in 0-30 cm sediment samples is given in Table 2.1. The concentration distribution of metals follows the decreasing order: Fe > Mn > Zn > Cr > Cu > As > Pb > Ni > Cd. Based on mean values, Fe (35,092.3 mg/kg) was the dominant metal in the sediment samples, followed by Mn (519.1) and Zn (477.9), while Cd showed the minimum mean (4.4 mg/kg) in the sediment samples. High standard deviation was found for Fe (46,087.0) and As (169.1) as a result of high concentration of these two metals in S7, located right before Thanh Liet Dam (Fig. 2.1). The dam closing/opening regime resulted in stagnation of water and sediment there in dry season, when samples were collected. The values of the Geo-accumulation Index (Table 2.1) were observed to be negative for Mn (-1.3), Fe (-1.0), Ni (-0.7) and Cr (-0.3), suggested that the sediment was not polluted by such four metals. Meanwhile, it was slightly polluted with Cu (0.4), and moderately with Pb (1.2) and Zn (1.8). The sediment was under of moderate to strong pollution with As due to high value of I_{geo} (2.1). Especially, the highest I_{geo} value of Cd (3.3) suggested the sediment was at strong pollution by this metal. In summary, the I_{geo} values of the nine heavy metals in sediment decreased in the order of Cd > As > Zn > Pb > Cu > Cr > Ni > Fe > Mn. By using Fe as normalizing element, Enrichment Factor (EF) indicated the similar order of metal pollution degrees as I_{geo} (Table 2.1). There were no enrichment of Mn (0.8) and Ni (1.3), minor enrichment for Cr (1.6) and Cu (2.62), while Pb (4.5) was at moderate enrichment level. Zn (6.8) and As (8.7) values fall within 5 and 10 suggesting the sediment was moderately severe enriched by those two metals. Amazingly, the EF value of Cd shot up to 19.9 indicating the severe enrichment of this metal in sediment. Even using Fe or Mn as normalizing element, the order and degree of enrichment (Sakan et al. 2009) for concerned metals in sediment were almost similar (Table 2.1). This indicated that beside using Fe, Si and Al, Mn can also be used as normalizing element in evaluating metal enrichment degree, especially for polluted urban rivers such as To Lich in Hanoi city.

Table 2.1. Heavy metal concentration (mg/kg) in 0-30 cm sediment, Enrichment Factor (EF), and Geo-accumulation Index (I_{geo})

Heavy metal	**Mn**	**Fe**	**Ni**	**Cr**	**Cu**	**Pb**	**Zn**	**As**	**Cd**
Min	311.1	15,323.5	23.9	77.1	35.1	33.2	305.2	19.3	0.8
Max	912.7	148,912.1	111.4	174.0	155.9	90.5	718.1	501.8	11.8
Mean	519.1	35,092.3	64.8	107.9	87.7	67.1	477.9	83.9	4.4
Standard deviation	182.9	46,087.0	27.9	29.8	40.1	19.8	145.4	169.1	4.3
Average shale[1]	850	47,200	68	90	45	20	95	13	0.3
I_{geo}	-1.3	-1.0	-0.7	-0.3	0.4	1.2	1.8	2.1	3.3
EF[2]	0.8	1.0	1.3	1.6	2.6	4.5	6.8	8.7	19.9
EF[3]	1.0	1.0	1.6	2.1	3.4	5.7	9.2	7.8	23.5

[1] World geochemical background value in average shale (Turekian and Wedepohl 1961).
[2] using Fe as normalizing element.
[3] using Mn as normalizing element.

In comparison with the sediment quality guidelines (SQGs), the concentrations of Zn and Cd (Table 2.2) were exceeding the maximum permissible concentrations for crops (Steve 1994). There are several pumping stations located along To Lich River, which may also pump sediment for enrichment agricultural field, negatively affecting on quality of agricultural products. It is also important to determine whether the concentration of heavy metals in sediment in this study poses a threat to aquatic life, since water of To Lich River is still used for aquaculture after discharging to Nhue River. The heavy metal concentrations found were compared with consensus-based threshold effect concentration (TEC) and probable effect concentration (PEC) values (MacDonald et al. 2000; Table 2.2). Mean values of Ni, Zn, and As exceeded the PEC, which likely result in adverse effects on aquatic life. Considering maximum concentrations (Table 2.1), values of six of seven concerned metals much exceeded (Table 2.2). These suggest that sediment from To Lich River is not suitable for both crops and aquaculture.

Table 2.2. Comparison of heavy metal concentration (mg/kg) in study area with sediment quality guidelines

Heavy metal	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
This study	107.9	519.1	35,092.3	64.8	87.7	477.9	83.9	4.4	67.1
SQG-unpolluted[1]	< 25	na	na	< 20	< 25	< 90	< 3	na	< 40
SQG-moderately polluted[1]	25-75	na	na	20-50	25-50	90-200	3-8	na	40-60
SQG-heavily polluted[1]	> 5	na	na	> 50	> 50	> 200	> 8	> 6	> 60
MPC[2]	400	na	na	110	200	450	-	3	300
TEC[3]	43.4	na	na	22.7	31.6	121.0	9.8	0.9	35.8
PEC[4]	111.0	na	na	48.6	149.0	459.0	33.0	4.9	128.0

[1] USEPA sediment quality guidelines (Pekey 2006a).
[2] Maximum permissible concentrations of potentially toxic heavy metal for crops (Steve 1994).
[3] Threshold effect concentration, [4] Probable effect concentration (MacDonald et al. 2000).
na data not available.

Table 2.3 summarizes the statistical data set of 0-10 cm water samples. The metal concentrations in water from To Lich River followed the order: Mn > Zn > As > Pb > Ni > Cu > Cr > Cd, which was dissimilar to that in sediment (Table 2.1). This indicated the distinct in the balance of heavy metals in aquatic and sedimentary systems (Varol and Sen, 2012). The speed of stagnation and dissolve of heavy metals were different depending much on water flow rate, metal concentrations, etc. (Marcus 1989; Martin 2000), which led to differences in concentration order of heavy metal in sediment and water. The highest metal concentration in water belonged to Mn (216.2 μg/L), followed by Zn (51.1), As (39.1), other metals (Pb, Ni, Cu, and Cr) with mean concentration of lower than 10μg/L. Cd was observed to have lowest concentration in the water samples with maximum value of 0.2 μg/L. Comparing to previous data (Table 2.3; CENMA 2008; Kikuchi 2009) on heavy metal contamination in water, concentration of Ni, Zn, As, and Pb tended to increase while that of Cr, Mn, and Cu decreased. This suggested that environment of To Lich River has been either not yet improved or improved not such much even several regulations on environment protection were issued recently.

Table 2.3. Heavy metal concentrations (μg/L) in water and mean concentration reported from previous studies

Heavy metal	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Min	2.0	83.7	5.0	3.0	28.0	13.1	na	6.0
Max	5.0	400.8	13.0	7.0	93.0	76.2	0.2	11.0
Mean	2.9	216.2	7.6	4.5	51.1	39.1	na	8.1
Standard deviation	1.4	87.1	2.6	1.7	20.2	18.1	na	1.6
Sample collected in rainy season 2008[1]	< 5.0	230.4	na	na	na	14.7	na	< 0.1
Sample collected in June 2006[2]	11.2	116.0	3.4	8.4	36.1	10.3	na	2.8
Sample collected in October 2005[2]	8.4	114.0	6.0	4.6	31.6	5.6	na	1.9

[1] CENMA (2008).
[2] Kikuchi et al. (2009).
na data not available.

Among eight concerned heavy metals in water (Table 2.4), Mn had the concentration exceeded the WHO (2006) maximum permitted level for irrigation water standard, even though it has been widely used for agriculture irrigation. Water of To Lich River has not been directly used for aquatic life, however after discharging to Nhue River it is used for aquaculture. Concentration of Ni, Cu, Zn, As, and Cd in water was still lower than permitted level for aquatic life (USEPA 2006).

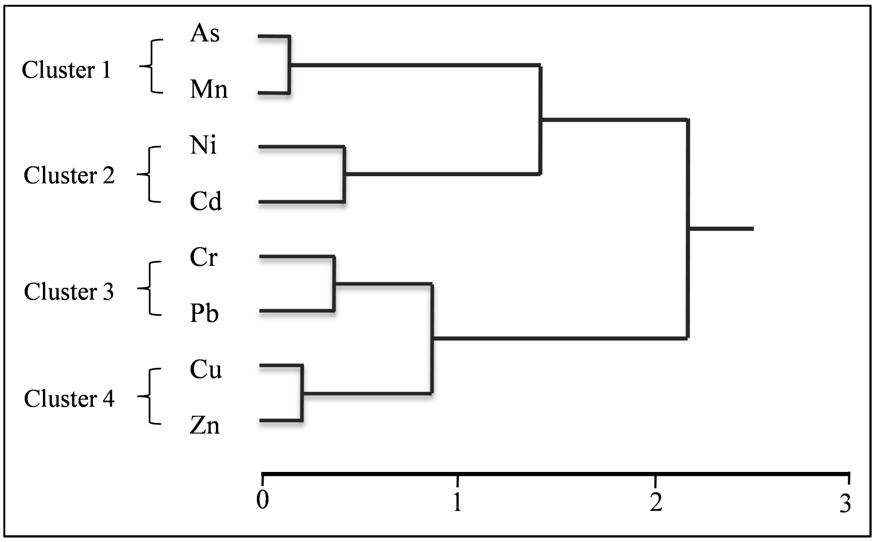
Table 2.4. Comparison of heavy metal concentration (μg/L) in study area with water quality guidelines

Heavy metal	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
This study	2.9	216.2	7.6	4.5	51.1	39.1	na	8.1
WHO[1]	100	200	200	200	2,000	100	10	5,000
USEPA[2]	na	na	470	13	120	340	2	na

[1] Irrigation water standard (WHO 2006).
[2] Acute values for protection of freshwater aquatic life (USEPA 2006).
na data not available.

2.3.2. Hierarchical cluster analysis

Cluster analysis (CA) was performed to identify relationships among metals and their possible sources (Casado-Martinez et al. 2009; Chung et al. 2011). Four clusters were observed (Fig. 2.2) for the metals in 0-30 cm sediment with significant linkage distance, indicating relatively high independency for each cluster. The first cluster was formed by As and Mn, which were derived from a mix of anthropogenic and lithogenic sources. Mn and As were extremely well correlated with each other presented by high correlation (r = 0.99; Table 2.5). Mn is found abundant in the Earth's crust (Turekian and Wedepohl 1961), however its concentration was higher at downstream site (S7; Fig. 2.1) after a complex of manufacturing plants. Therefore, Mn can be from both natural and anthropogenic sources. As, the redox sensitive element, is commonly more soluble in oxidized groundwater occurring as oxyanion or in the form of AsO_4^{2-} or $H_2AsO_4^-$ (Chen et al. 2007). However, in reducing waters, As tends to be incorporated in insoluble minerals (Welch et al. 1998). Cluster 2 contained Cd and Ni, which were moderately correlated (r = 0.57). These two metals were mainly derived from anthropogenic sources (e.g. inorganic fertilizer application, mechanical engineering). Cluster 3 containing Cr and Pb, and cluster 4 containing Cu and Zn were derived from anthropogenic sources (e.g. vehicle fumes, leather manufacture), which were also confirmed by relatively strong correlations (Table 2.5). The order of significance of clusters was following: Cluster 1 > Cluster 4 > Cluster 3 > Cluster 2 (Fig. 2.2).



Linkage distance (Pearson)

Fig. 2.2 Dendrogram of specified metals in 0-30 cm sediment using Ward's method

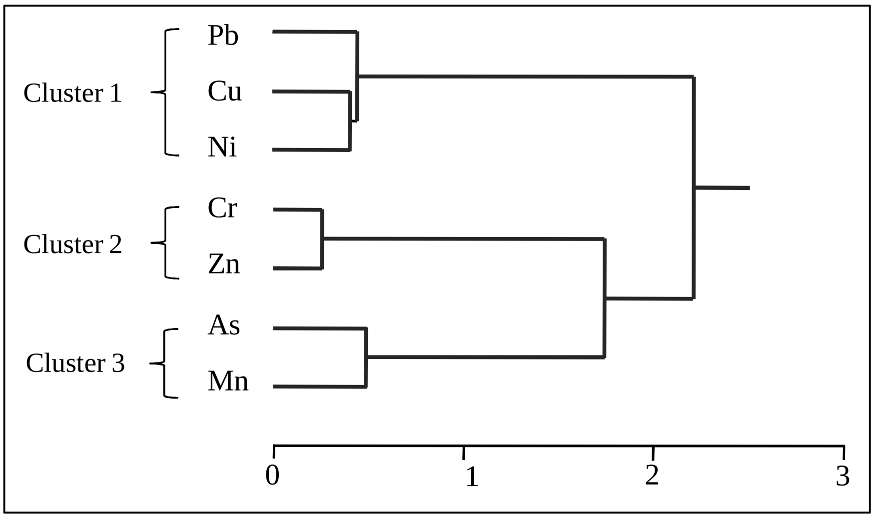
Fig. 2.3 illustrates the dendrogram of metals in water samples with three main clusters. The strong correlation between Cr and Zn (r = 0.75) was observed in the second cluster. Cu and Ni (r = 0.60), which well correlated with each other, were associated with Pb to form the first cluster. The third cluster was formed by As and Mn (r = 0.51). The inter-element correlations in each cluster were relatively weaker than that in sediment, representing by linkage distances in Fig. 2.2 and Fig. 2.3. The elements grouped in each cluster in water and that in sediment were also different, except correlated pair formed by As and Mn. Long history of sedimentation (Martin 2000), the difference of amount and component of wastewater discharged to To Lich River by years, seasons and manufacture's working schedules, water flow rate, and opening regime of Thanh Liet Dam (Fig. 2.1) responded for the such differences.

Table 2.5. Statistical results of factor analysis for 0-30 cm sediment

Matrix to be factored								
	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Cr	1							
Mn	0.03	1						
Ni	0.12	0.47	1					
Cu	0.49	0.04	0.37	1				
Zn	0.27	-0.37	0.09	**0.79**	1			
As	-0.17	**0.85**	0.09	-0.25	-0.48	1		
Cd	0.08	0.22	**0.57**	-0.10	-0.27	-0.19	1	
Pb	**0.62**	**0.59**	0.41	**0.70**	0.21	0.36	-0.03	1

Rotated loading matrix (VARIMAX Gamma=1.000)			
	PC1	PC2	PC3
Cu	**0.96**[1]	-0.08	0.05
Pb	**0.78**[1]	**0.57**[2]	0.10
Zn	**0.75**[1]	-0.46	-0.18
Cr	**0.69**[2]	0.01	0.11
As	-0.18	**0.96**[1]	-0.15
Mn	0.07	**0.93**[1]	0.29
Cd	-0.15	-0.07	**0.95**[1]
Ni	0.33	0.23	**0.80**[1]
Eigenvalues	2.72	2.39	1.70
% total variance	33.96	29.92	21.20
Cumulative %	33.96	63.88	85.08

Values in bold are statistically significant at $p < 0.05$. [1] Strong positive loadings (values > 0.7), [2] Moderate positive loading (0.5 < values < 0.7).



Linkage distance (Pearson)

Fig. 2.3 Dendrogram of specified metals in 0-10 water using Ward's method

2.3.3. Principal component analysis

Principal component (PC) analysis is applied to quantitatively evaluate the clustering behavior with Varimax normalization. According to Cattell and Jaspers (1967), PCs with eigenvalue > 1 were retained. The results for heavy metal contents in 0-30 cm sediment are given in Table 2.5 and Fig. 2.4. Three factors were originated with a cumulative variance of 85%. The first factor (PC1) contributed 34% of total variance, showing strong positive loadings on Cu (0.96), Pb (0.78) and Zn (0.75), and moderate positive loadings on Cr (0.69; Table 2.5). This association may be attributed to local industrial effluents. Cu may result from mechanical engineering and Cu-based agrochemicals/ phosphate fertilizers, which was presented by cluster of Cu and Zn (Fig. 2.2). Zn and its compounds have been used in different manufactured goods (e.g. paint, rubber/automobile tires) and in fertilizers applied in agriculture in river catchment. Chromium salt may be used in leather processing, which is located near S1 (Fig. 2.1), thus the effluents may contain high levels of Cr. Meanwhile, paint industry located near S6 (Fig. 2.1) could also be considered as one of pollution sources. The second factor (PC2) accounted for 30% of the total variance and contained As (0.96), Mn (0.93) and Pb (0.57; Table 2.5); thus covering metals originated from both natural and anthropogenic sources. The occurrence of Mn may be due to its common presence in the basic rock, since the concentration of this element was lower than background values ($I_{geo} < 0$; Table 2.1). As is well correlated with Mn ($r = 0.85$) as shown in correlation matrix (Table 2.5) and cluster analysis (Fig. 2.2), suggesting that As may originate from parent materials as well. In addition, As also originates from anthropogenic source, since arsenate and arsenite are utilized in production of dye stuffs and a preservative of leather products (Japan Environmental Sanitation Center 2005). Meanwhile, the presence of Pb in PC2 may suggest a source of vehicular fumes, since before 2007 gasoline blended with lead was widely used in Vietnam (Fig. 2.4). The third factor (PC3), explaining 21% of total variance, contained a high loading on Cd (0.95) and Ni (0.80), which had their origin mainly in industrial sources. This corresponded to cluster 2 (Fig. 2.2). As mentioned previously, using phosphate fertilizers was an important source of heavy metals to To Lich River sediment including Cd. Other sources of Cd may include other inorganic fertilizers (e.g. nitrogen or potash), atmospheric deposition or anthropic wastes such as sewage sludge, wastewater or waste materials. Ni originated from mechanical engineering, since it is an alloying metal. It may also come from untreated wastewater from nearby. In general, the results of principal component analysis (Table 2.5) have shown to be coincided with cluster analysis (Fig. 2.2) for 0-30 cm sediment.

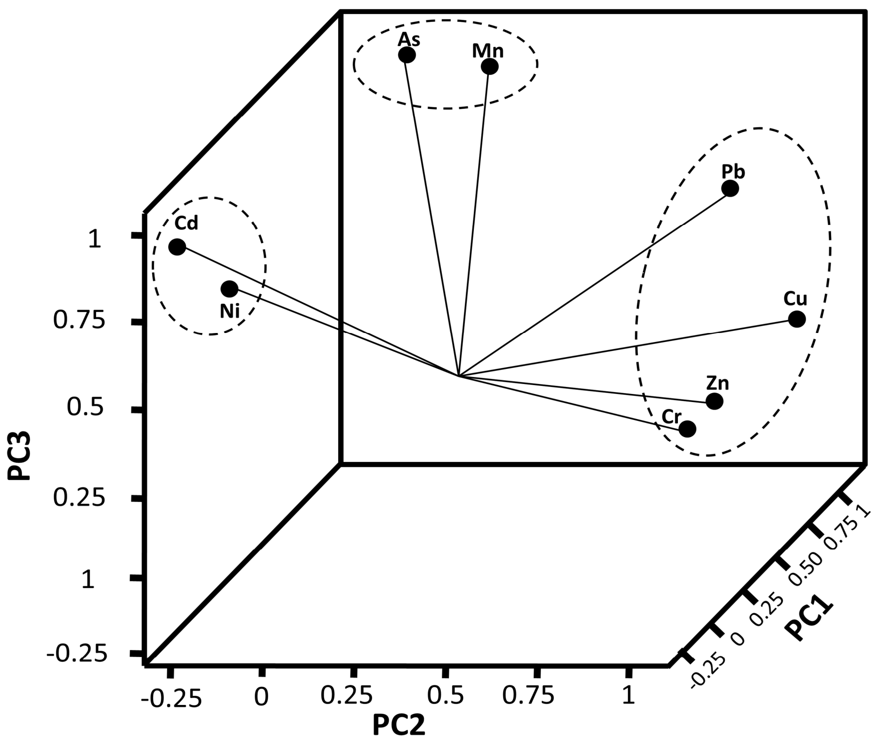


Fig. 2.4 Loading plots of principal component analysis for the three rotated components

For water data set, three factors were observed with a cumulative variance of 80%. PC1 was responsible for 31% variance and is best represented by Cu, Pb, and Ni with loadings of 0.90, 0.83 and 0.77, respectively. PC2 contained Zn (0.94) and Cr (0.92), accounting for 27% variance. The metals belonged to PC1 and PC2 mainly derived from anthropic wastes discharged into river. Meanwhile, As (-0.94) and Mn (-0.76) showed strong negative loadings in PC3 with total variance of 22%.

2.4. CONCLUSIONS

Heavy metal assessment and source discrimination are important for environmental improvement and protection strategy, especially for urbanizing cities as Hanoi, Vietnam. To Lich is one of the four main rivers, discharging three fourth wastewater in inner Hanoi city. The water of this river is not suitable for irrigation since Mn concentration was exceeding permitted concentration standard, while concentrations of As, Cd and Zn in sediment were likely to have adverse effects on agriculture and aquatic life. It is concluded that environment of To Lich River has not yet been improved even several regulations on environmental protection had been issued recently.

Principal component analysis indicated that As and Mn originated from both anthropogenic and natural sources, while Cu, Cr, Cd, Ni and Zn were mainly from local industrial influence, and Pb was from vehicular fumes. However, the ratio of source of heavy metals (e.g. mechanical engineering, rubber, soap, leather, hospital), which may support local government in issuing suitable environmental protection regulations and countermeasures, was not covered in this studied.

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CHAPTER 3. AN ASSESSMENT OF HEAVY METAL POLLUTION AND EXCHANGE BETWEEN WATER AND SEDIMENT SYSTEM IN THE TO LICH RIVER, INNER HANOI CITY

Has been under review by ***CATENA.***

ABSTRACT

The To Lich River (TLR) serves as a main receptor of wastewater from Hanoi inner city and supplying irrigation water for downstream areas. With the urbanization in recent decades, untreated and/or partially treated wastewater from both industry and household has been discharged to river leading to serious environmental problems. Heavy metal concentrations in surface water and different sediment layers at nine sampling positions along TLR were analyzed. Enrichment factor, Geo-accumulation index (GI), cluster analysis, and quality guidelines were used to assess current status and possible risks that may arise from heavy metal contamination. Mn concentration in surface water exceeded the irrigation water limit at seven of nine sites. Meanwhile, Cd was the most contaminated metal causing heavy sediment

Keywords: Cluster analysis, Geochemical indices, Metal accumulation, Quality guidelines, Sediment

3.1. INTRODUCTION

Heavy metal contamination in environment is of major concern because of their toxicity and threat to human life and the environment (Purves 1985).The majority of chemicals discharged into river system eventually end up in sediments that may act as a sink as well as a source of pollution (Beg and Ali 2008). Vegetables irrigated with heavy metal contaminated water increase heavy metal accumulation in their edible portions (Butt et al. 2005; Sharma et al. 2007; Kiziloglu et al. 2008). In addition, heavy metal contaminated sediments have negative effects on root and shoot growth of crops (Beg and Ali 2008). Disposal of dredged contaminated sediments may affect the surrounding environment due to the presence of harmful organic compounds and trace metals (Singh et al. 2000). Meanwhile, long-term leaching and migration of contaminants from improperly disposed sediment as on river banks and floodplain can result in contamination of both surface and ground water (Maskell and Thornton 1998). Therefore, sediment quality is an important focus in the assessment, protection, and management of aquatic ecosystems. Because it affects the fate of many chemicals, which are potential impacts on organisms exposed to sediments with elevated chemical concentrations (Smith et al. 1996).

It is frequently said that humic substances play a major role in controlling the behavior and mobility of metals in sediment, that are essential trace elements or pollution-derived heavy metals (Livens 1991). Organic matter exists as dissolved and suspended forms, and/or in the bottom sediments. Those forms of the organic matter interact with heavy metals (Mulligan and Yong 2006). Sediments containing high amounts of organic matter tend to accumulate higher metal levels (Facetti et al. 1998; Nguyen et al. 2010), because their compounds have pronounced metal binding properties (Bolt and Bruggenwert 1976). Heavy metal concentrations tended to decrease with the increase of sediment depth, meanwhile Pb, Zn, and Cr contents tended to increase toward downstream distance (Subramanian et al. 1987).

Several studies (Ho and Egashira 2000; Nguyen et al. 2008, 2010) on quality of river water and sediment in inner city of Hanoi indicated that heavy metal concentration exceeded the maximum permissible concentrations for agriculture. However, that in water of To Lich River (TLR) was lower than Vietnamese surface water standard (Kikuchi et al. 2009). Those indicate the complexity of heavy metal contamination in TLR. The fact that resources of TLR are still being used for agriculture and there is a dense population living near river bank, which became playground. Regular study on contamination degree of water and sediment is needed to direct the use of resources and a proper management scheme for TLR basin. Thus, the aims of this work are (1) to determine heavy metal concentration and distribution in water and sediment of the TLR and (2) to assess degree and extent of metal contamination in the river using statistical approaches and quality guidelines.

3.2. MATERIALS AND METHODS

3.2.1. Description of study area

The To Lich River (TLR) is one of four main rivers in inner city of Hanoi; those rivers receive and discharge 451,000 m^3 water/day including industrial, household, and hospital wastewaters (Nguyen 2005). TLR starts from West Lake in North Hanoi, running through residential areas in upstream and industrial area in downstream before discharging to Nhue River in South Hanoi (Fig. 3.1). The River has a length of approximate 17 km and covers a basin area of 20 km^2. The first 3.1 km from upstream of TLR (between sampling position 1 and 2 in Fig. 3.1) has not been embanked, while the embankment at downstream was finished in 2002 except the section between sampling position 6 and 7 (Fig. 3.1) because of difficulty in land clearance. As a result of embankment, the river has a width of 20-45 m, depth of 2-4 m, and maximum flow capacity of 30 m^3/s. There are 239 point sources, including pipe culverts sized from 300 to 1,800 mm in diameter and box culverts sized from 1,200 x 1,200 mm to 3,300 x 3,300 mm, discharging wastewater to TLR (Nguyen 2005). Non-point sources are also available, which is the illegal dumping of domestic and construction waste on river bank or directly to river. Wastewater discharged to TLR amounts 290,000 m^3/day, accounted for 64% of total wastewater in the city. Sixty percent of 290,000 m^3 generated from industry, 2,000 m^3 was from hospitals, and the remaining amount was household wastewater (HENRD 2003). In dry season, water discharged from West Lake is limited because of low water level; most water in TLR is wastewater from households and industry with low flow rate and high pollution (HENRD 2009).

There are 33 manufacturing plants discharging wastewater to TLR without appropriate treatment (EIO 2001), except 4.4% (Nguyen 2005). Thirty of those plants are from Thuong Dinh - Nguyen Trai Industrial Zone, which discharge wastewater to 9-16 km downstream section of the river; including 14 enterprises of mechanical industry, four of textile industry, three of leather industry, two of chemical industry (rubber and soap), two of ceramic industry, one of food processing industry (tobacco), one of paper industry, and three other enterprises.

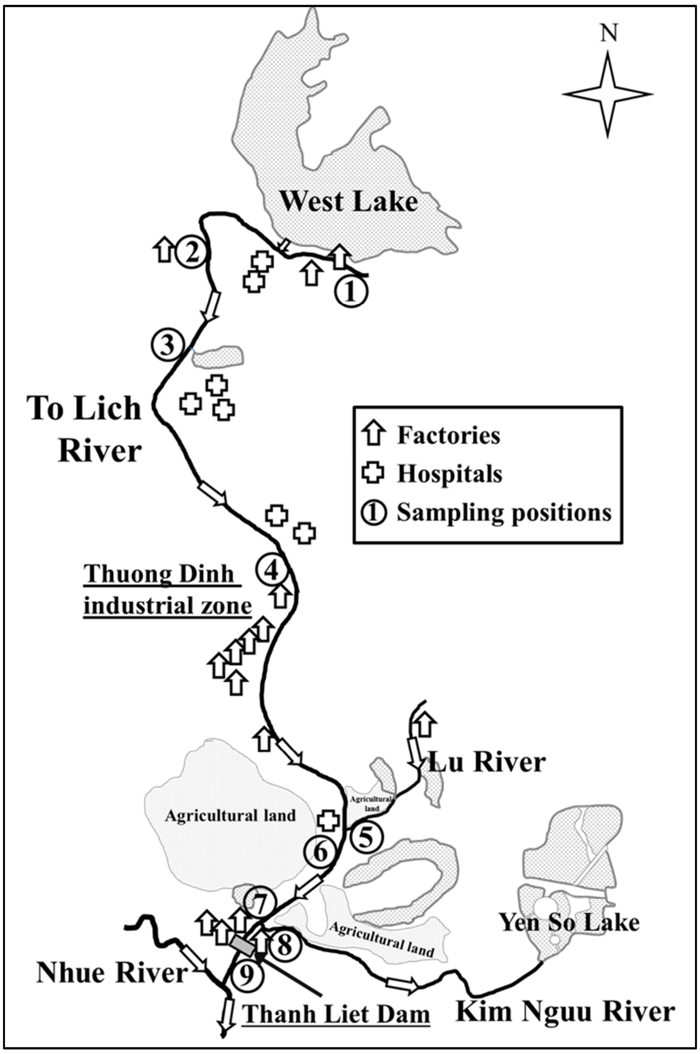


Fig. 3.1 The sites of sampling position

At 0.5 km from downstream (Fig. 3.1), Thanh Liet Dam, which has maximum water level of 4.5 m and discharge capacity of 45 m^3/s, was built to control water flow direction of TLR. In general, when water level of Nhue River is lower than that of TLR the dam is open. Conversely the dam is closed, when water of TLR is in low level and/or too polluted it may affect the aquaculture in downstream of Nhue River. In such case, water runs to Yen So Lake through Kim Nguu River (Fig. 3.1) and then it is pumped to Hong River.

3.2.2. Sample collection

Water (at 10 cm depth) and sediment of different depths (0-30, 30-60, 60-90, and 90-120 cm) were collected at nine positions along the river (Fig. 3.1). The distances from upstream to sampling positions are shown in Table 3.1. The first sampling position was located at 0.2 km from West Lake in un-embankment section. Sampling positions 2, 3, and 4 were at embanked section, mostly receiving household and hospital wastewaters. The remaining sampling positions receive various types of wastewater including industrial effluents. Position 5 was located at intersection, where Lu River discharges to TLR, meanwhile positions 6 and 7 were at the un-embankment section of TLR. Position 8 was located at intersection between Kim Nguu River and TLR, and position 9 was located below Thanh Liet Dam at 0.4 km from downstream (Fig. 3.1). All samples were collected in dry season in March 4-5, 2011.

Water samples were collected in polypropylene bottles and stored at 4^oC in refrigerator until analysis. For heavy metal determination, the water samples were acidified with conc. HNO_3 to pH < 2 (1.5 ml conc. HNO_3 per liter of sample). The pH of water was measured in situ using a portable pH meter. Sediment samples, on the other hand, were taken from river bed using a self-made sediment sampler and put into polyethylene bottles**.**

3.2.3. Chemical analysis

Total organic carbon (TOC) contents in water and sediment were analyzed using a TOC analyzer (TOC-5000A, Shimadzu). For heavy metal analysis, sediment samples were air-dried at room temperature and passed through 1mm stainless steel sieve to remove big particles. Then the samples were heated in an oven at 60^oC until constant weight, powdered and homogenized. As for microwave-assisted acid digestion procedure, approximately 50 mg dry homogenized sediment was placed in a vessel and successively digested with 10 mL of conc. HNO_3 in a microwave digestion system (USEPA 2007)**.** After cooling, the digest was transferred into a plastic volumetric flask and adjusted to 50 mL volume with Mili-Q water. The sample was finally filtered through a membrane filter **(**0.45 μm pore size). Metal **c**oncentrations (Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb) in water and acid-digested sediment samples were determined using ICP-MS.

Standard operating procedures, calibration with standards, and analysis of reagent blanks, and analysis of replicates were used to guarantee the quality of analytical data. Analysis for all samples was carried out in triplicate to get the mean as final data.

3.2.4. Sediment contamination assessment

3.2.4.1. Enrichment factor

Enrichment factor (EF) was calculated using the following equation (Eq. 3.1):

$$EF = \frac{(Metal/Fe)_{sample}}{(Metal/Fe)_{background}} \quad (3.1)$$

in which, $(Metal/Fe)_{sample}$ is the ratio of metal to Fe in the sediment samples and $(Metal/Fe)_{background}$ is the ratio of natural background value of the corresponding metal to Fe. As background values of the metals of concern in current study site are not available, the earth crust values (Turekian et al. 1961) were used (Singh et al. 2005).

3.2.4.2. Geo-accumulation index

The calculation of Geo-accumulation index (GI) was following equation 3.2 (Eq. 3.2)

$$GI = Log_2 \frac{C_n}{1.5B_n} \quad (3.2)$$

where C_n is the concentration of metal n in sediment in this study and B_n is the geochemical background concentration of the corresponding metal . The background values were similar as those used in Enrichment factor calculation. Figure 1.5 is the background matrix correction factor due to lithospheric effects (Memet and Bulent 2012).

3.2.4.3. Sediment quality comparison

The quality of sediment of each sampling position was evaluated using the consensus-based sediment-quality guidelines (SQGs), which assess possible risk to aquaculture from the heavy metal contamination. Guidelines consist of a threshold effect concentration (TEC) below which adverse effects are not expected to occur and a probable effect concentration (PEC) above which adverse effects are expected to occur more often (MacDonald et al. 2000). Meanwhile, mean PEC quotients were calculated by methods of Long et al. (1998; i.e., for sediment sample, the average of the ratios of concentration of each contamination to its corresponding PEC was calculated for each sampling position). Sediment is predicted to be not toxic if mean PEC quotient is < 0.5. In contrast, it is predicted to be toxic when mean PEC quotient exceeds 1.5 (MacDonald et al. 2000).

Sediment quality in this study was also compared with that of other rivers around the world to see the extent of metal pollution in the To Lich River.

3.2.4.4. Statistical analysis

All statistical analyses were done with statistical significance set at $p < 0.05$. Cluster analysis (CA) was employed to classify all nine sampling positions into different clusters, based on their nearness or similarity (Varol and Şen 2009). In this study, CA was performed on the data set using Ward's method with Euclidean distances as a measure of similarity (Ward 1963).

3.3. RESULTS AND DISCUSSION

3.3.1. Sediment

3.3.1.1. Total organic carbon and heavy metal concentration in sediment

Total organic carbon (TOC) in sediments ranged from 0.5 to 9.7% (Table 3.1), while concentration of Cr ranged from 55.1 to 805.6 mg kg^{-1}, 267.7 - 1,649.9 for Mn, 9,337 - 187,572 for Fe, 23.3 - 206.7 for Ni, 35.1 - 210.4 Cu, 143.8 - 1,502 for Zn, 14 - 824.5 for As, 0.8 - 105.2 for Cd, and from 33.2 to 155.5 mg kg^{-1} for Pb. There was no significant relationship between TOC or heavy metal level and downstream distances (Table 3.1) as well as sediment depths (Fig. 3.2). The concentration of heavy metals was observed to be decreased by sediment depths and increase toward downstream distance in Ganges and Brahmaputra Rivers of India (Subramanian et al. 1987) and in sedimentary basin of Finland (Vallius 1999) as a result of gradual accumulation of heavy metals from industrial and agriculture sources. This study is different, since the To Lich River is quite short (approximate 17 km) and higher water flow rate therefore wastewater may take only a few days to flow down to Nhue River through Thanh Liet Dam (Fig. 3.1). The same phenomenon was concluded by Pease et al. (2007) for study in Tar River floodplain that downstream correlations for heavy metals were not found.

Table 3.1. Concentration of heavy metals (mg kg^{-1}), total organic carbon (TOC, %), and mean probable effect concentration quotients (mPECq) for each sampling position in the To Lich River, Hanoi

Sampling position	Distance from upstream (km)	Sediment depth (cm)	TOC	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb	mPECq
S1	0.2	0-30	4.9	55.1	1,354.5	187,572.6	70.4	106.9	593.7	824.5	1.2	106.2	4.0
		30-60	3.8	82.3	1,398.4	157,842.2	93.4	147.8	512.9	677.5	1.5	155.5	
		60-90	4.1	66.8	1,649.9	164,753.1	63.2	130.3	702.8	705.8	1.4	152.7	
S2	3.1	0-30	4.1	174.0	455.1	16,125.0	48.3	125.2	568.1	24.9	1.1	90.5	0.9
		30-60	4.6	186.4	378.7	11,651.2	50.9	98.9	427.0	16.9	0.8	59.1	
		60-90	5.8	217.0	319.3	9,443.0	45.5	82.0	478.3	19.1	0.9	66.0	
		90-120	4.8	338.6	414.9	15,338.8	60.9	108.2	580.3	25.3	1.2	88.1	
S3	5.1	0-30	3.7	98.1	499.4	15,323.5	62.7	156.0	718.1	19.3	1.9	82.3	1.1
		30-60	3.1	181.2	706.8	26,479.9	90.5	146.6	784.8	28.1	2.7	99.6	
		60-90	3.5	163.1	662.5	24,084.7	83.3	154.6	881.4	26.9	2.4	98.5	
		90-120	3.1	136.5	574.9	20,984.9	73.1	129.8	698.1	24.6	2.2	81.3	
S4	9.1	0-30	4.7	107.9	528.4	17,809.9	111.4	112.5	609.5	21.1	6.4	64.0	2.1
		30-60	8.1	173.1	524.0	21,919.3	102.3	210.4	1,212.4	48.5	105.2	124.3	
		60-90	5.1	141.3	434.0	18,066.6	107.0	140.3	769.6	27.2	20.7	103.9	
		90-120	6.4	91.4	267.7	9,337.2	72.7	95.6	540.9	18.9	9.0	76.8	
S5	13.6	0-30	2.7	77.1	350.7	16,590.7	44.3	59.5	354.8	19.8	0.8	49.4	1.8
		30-60	4.7	805.6	477.0	24,206.1	206.7	189.5	1,502.0	68.2	3.6	97.5	
		60-90	3.7	587.6	500.5	22,590.4	179.2	151.7	1,026.8	43.3	2.2	88.8	

Table 3.1 (Continued)

S6	13.8	0-30	2.0	118.1	520.7	24,073.3	92.9	81.7	408.9	21.3	9.7	74.0	0.7
		30-60	1.0	78.1	567.8	19,719.9	62.2	52.5	212.8	14.9	1.6	56.0	
		60-90	0.5	74.0	627.5	23,535.2	51.1	39.1	143.8	14.0	0.8	46.0	
S7	15.5	0-30	1.7	108.2	574.4	21,313.4	62.9	66.3	356.9	20.5	11.8	57.3	1.1
		30-60	2.2	157.2	503.1	21,857.2	77.5	81.8	468.1	26.8	14.5	68.6	
S8	15.7	0-30	2.6	95.5	912.6	148,912.1	72.6	65.3	305.2	501.8	2.5	85.7	1.8
		30-60	1.7	72.7	753.0	28,451.6	56.9	50.0	192.2	44.8	1.9	64.6	
S9	16.3	0-30	9.7	84.8	311.1	20,590.1	23.3	35.1	502.1	42.0	1.2	33.2	0.6

mPECq < 0.5, sampling positions are predicted to be not toxic to aquaculture life; mPECq > 1.5, they are predicted to be toxic (Macdonald et al. 2000).

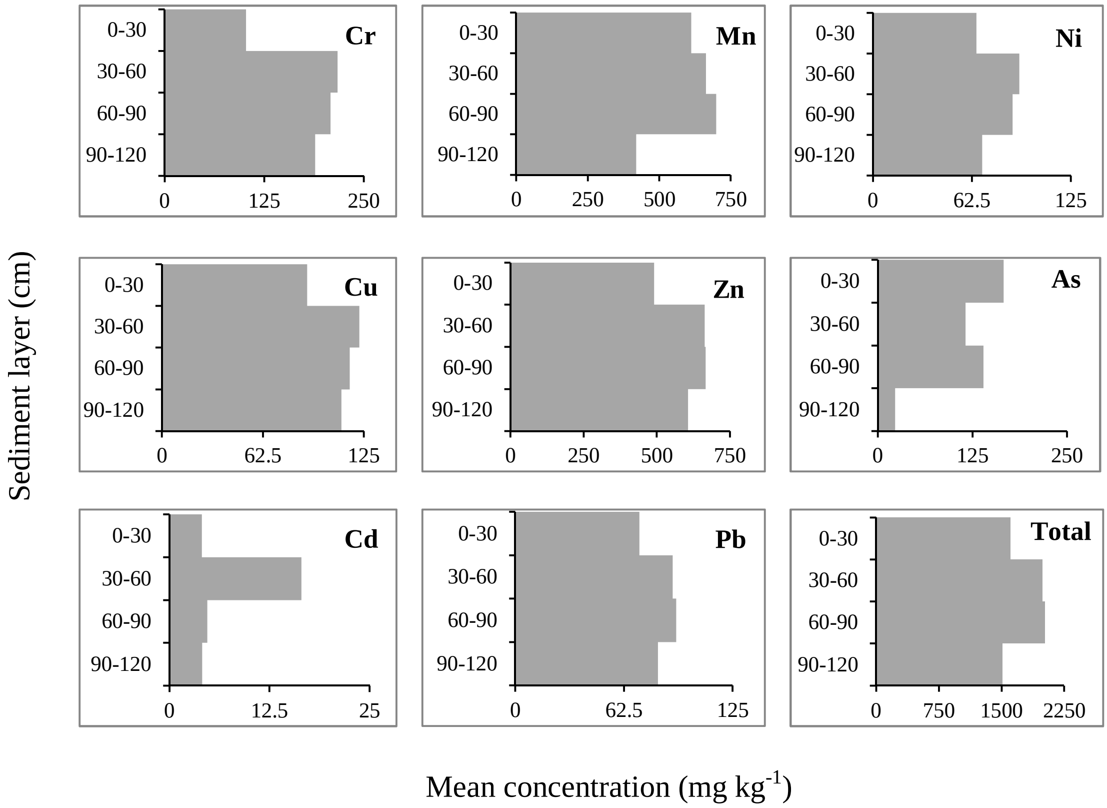


Fig. 3.2 Relationship between sediment depth and mean concentration of heavy metal

3.3.1.2. Contamination indices

Enrichment factor (EF) and Geo-accumulation index (GI) were matching in explaining contamination degrees of heavy metals in this study (Table 3.2). Generally, if EF values were lower than 5 (moderate enrichment) then corresponding values of GI were lower than 3 (moderately contaminated). The lowest contaminated metal was Mn for all sediment layers, which owned EF values of 0.3-1.9 (no or minor enrichment) corresponding to GI values of minus 2.3 to 0.4 (uncontaminated). Meanwhile, Cd was the highest contaminated metal with GI value of 7.9, corresponding to EF value of 754.8 (Table 3.2). There were no metals causing heavily contaminated at all sampling positions (Table 3.2; Fig. 3.3). Except Mn and Fe, all other heavy metals caused contamination at some extents for specific sampling positions and/or sediment layers. Pb caused moderate to heavy contamination for 11.5% of sediment samples, Zn caused 34.6% samples moderate to heavy contamination and 7.7% samples heavy contamination, and As caused 3.8 and 11.5% samples heavy to extreme contamination and extreme contamination, respectively. Meanwhile, 89% samples were contaminated with Cd at moderate to extreme level (Fig. 3.3). There were two sampling position S1 and S4 (Table 3.2) under extreme contamination based on maximum GI value, three under heavy to extreme (S6, S7, and S8), while S5 were under heavy, S3 under moderate to heavy, and S2 and S9 under moderate contamination. Patterns of relationship between heavy metal contamination degree (GI) and downstream distance and/or sediment depths were also not found, indicating the dynamics of heavy metals, water regime, etc., of the To Lich River.

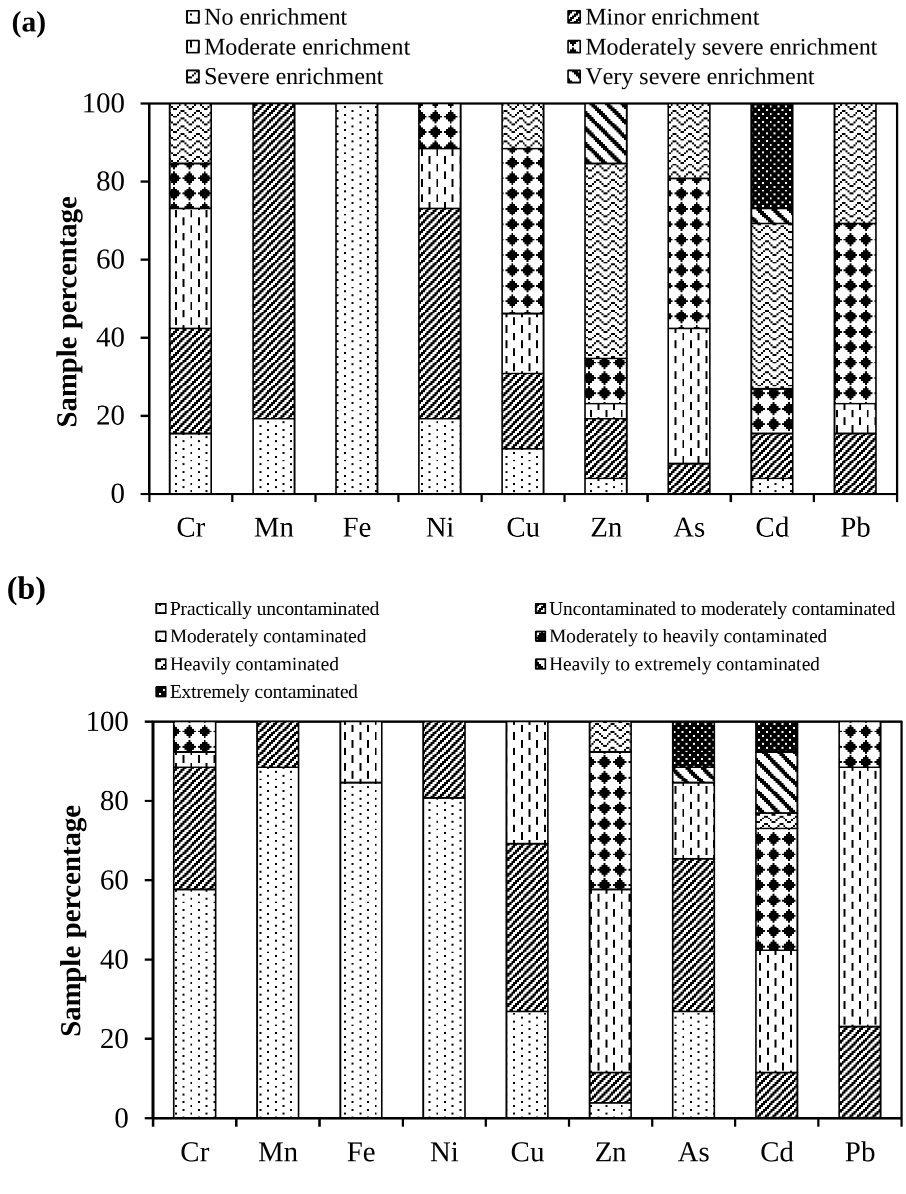


Fig. 3.3 Percentage of samples of enrichment (a) and of geo-accumulation (b) classes

Table 3.2. Enrichment factor (EF) and Geo-accumulation index (GI) of heavy metals for sediments in the To Lich River, Hanoi, using Fe as background value

Sampling position	**Sediment depth (cm)**	**Cr**		**Mn**		**Fe**		**Ni**		**Cu**		**Zn**		**As**		**Cd**		**Pb**		**Contamination level**[a]
		EF	*GI*	*EF*	*GI*	*EF*	*GI*	*EF*	*GI*	*EF*	*GI*	*EF*	*GI*	*EF*	*GI*	*EF*	*GI*	*EF*	*GI*	
S1	0-30	0.2	-1.3	0.4	0.1	1.0	1.4	0.3	-0.5	0.6	0.7	1.6	2.1	16.0	**5.4**	1.0	1.4	1.3	1.8	extreme
	30-60	0.3	-0.7	0.5	0.1	1.0	1.2	0.4	-0.1	1.0	1.1	1.6	1.8	15.6	5.1	1.5	1.8	2.3	2.4	
	60-90	0.2	-1.0	0.6	0.4	1.0	1.2	0.3	-0.7	0.8	0.9	2.1	2.3	15.6	5.2	1.3	1.6	2.2	2.3	
S2	0-30	5.7	0.4	1.6	-1.5	1.0	-2.1	2.1	-1.1	8.1	0.9	17.5	**2.0**	5.6	0.4	10.6	1.3	13.2	1.6	moderate
	30-60	8.4	0.5	1.8	-1.8	1.0	-2.6	3.0	-1.0	8.9	0.6	18.2	1.6	5.3	-0.2	11.2	0.9	12.0	1.0	
	60-90	12.0	0.7	1.9	-2.0	1.0	-2.9	3.3	-1.2	9.1	0.3	25.2	1.7	7.3	0.0	15.7	1.1	16.5	1.1	
	90-120	11.6	1.3	1.5	-1.6	1.0	-2.2	2.8	-0.7	7.4	0.7	18.8	2.0	6.0	0.4	12.2	1.4	13.6	1.6	
S3	0-30	3.4	-0.5	1.8	-1.4	1.0	-2.2	2.8	-0.7	10.7	1.2	23.3	2.3	4.6	0.0	19.7	2.1	12.7	1.5	moderate to heavy
	30-60	3.6	0.4	1.5	-0.9	1.0	-1.4	2.4	-0.2	5.8	1.1	14.7	2.5	3.9	0.5	15.8	**2.6**	8.9	1.7	
	60-90	3.6	0.3	1.5	-0.9	1.0	-1.6	2.4	-0.3	6.7	1.2	18.2	2.6	4.0	0.5	15.8	2.4	9.6	1.7	
	90-120	3.4	0.0	1.5	-1.1	1.0	-1.8	2.4	-0.5	6.5	0.9	16.5	2.3	4.3	0.3	16.2	2.3	9.1	1.4	
S4	0-30	3.2	-0.3	1.6	-1.3	1.0	-2.0	4.3	0.1	6.6	0.7	17.0	2.1	4.3	0.1	56.7	3.8	8.5	1.1	extreme
	30-60	4.1	0.4	1.3	-1.3	1.0	-1.7	3.2	0.0	10.1	1.6	27.5	3.1	8.0	1.3	754.8	**7.9**	13.4	2.1	
	60-90	4.1	0.1	1.3	-1.6	1.0	-2.0	4.1	0.1	8.1	1.1	21.2	2.4	5.5	0.5	180.4	5.5	13.6	1.8	
	90-120	5.1	-0.6	1.6	-2.3	1.0	-2.9	5.4	-0.5	10.7	0.5	28.8	1.9	7.4	0.0	151.1	4.3	19.4	1.4	
S5	0-30	2.4	-0.8	1.2	-1.9	1.0	-2.1	1.9	-1.2	3.8	-0.2	10.6	1.3	4.3	0.0	7.8	0.9	7.0	0.7	heavy
	30-60	17.5	2.6	1.1	-1.4	1.0	-1.5	5.9	1.0	8.2	1.5	30.8	**3.4**	10.2	1.8	23.4	3.0	9.5	1.7	
	60-90	13.6	2.1	1.2	-1.3	1.0	-1.6	5.5	0.8	7.0	1.2	22.6	2.8	7.0	1.2	15.3	2.3	9.3	1.6	

Table 3.2 (Continued)

S6	0-30	2.6	-0.2	1.2	-1.3	1.0	-1.6	2.7	-0.1	3.6	0.3	8.4	1.5	3.2	0.1	63.5	**4.4**	7.3	1.3	heavy to extreme
	30-60	2.1	-0.8	1.6	-1.2	1.0	-1.8	2.2	-0.7	2.8	-0.4	5.4	0.6	2.7	-0.4	13.1	1.9	6.7	0.9	
	60-90	1.6	-0.9	1.5	-1.0	1.0	-1.6	1.5	-1.0	1.7	-0.8	3.0	0.0	2.2	-0.5	5.2	0.8	4.6	0.6	
S7	0-30	2.7	-0.3	1.5	-1.2	1.0	-1.7	2.0	-0.7	3.3	0.0	8.3	1.3	3.5	0.1	87.0	4.7	6.3	0.9	heavy to extreme
	30-60	3.8	0.2	1.3	-1.3	1.0	-1.7	2.5	-0.4	3.9	0.3	10.6	1.7	4.4	0.5	104.7	**5.0**	7.4	1.2	
S8	0-30	0.3	-0.5	0.3	-0.5	1.0	1.1	0.3	-0.5	0.5	0.0	1.0	1.1	12.2	**4.7**	2.7	2.5	1.4	1.5	heavy to extreme
	30-60	1.3	-0.9	1.5	-0.8	1.0	-1.3	1.4	-0.8	1.8	-0.4	3.4	0.4	5.7	1.2	10.6	2.1	5.4	1.1	
S9	0-30	2.2	-0.7	0.8	-2.0	1.0	-1.8	0.8	-2.1	1.8	-0.9	12.1	**1.8**	7.4	1.1	8.9	1.4	3.8	0.1	moderate

GI ≤0 is practically uncontaminated, 0<GI≤1 is uncontaminated to moderate, 1<GI≤2 is moderate, 2<GI≤3 is moderate to heavy, 3<GI≤4 is heavy, 4<GI≤5 is heavy to extreme, and GI>5 is extremely contaminated.

EF 1≤ indicates no enrichment, 1<EF≤3 is minor, 3<EF≤5 is moderate, 5<EF≤10 is moderately severe, 10<EF≤25 is severe, 25<EF≤50 is very severe, and EF>50 is extremely severe enrichment.

[a] based on highest value of GI at each sampling position.

Bold and underline numbers are highest values of GI corresponding to each sampling position.

3.3.1.3. Sediment quality comparison

Comparing heavy metal data set of the To Lich River (TLR) with that of other rivers around the world (Table 3.3), the result indicated that degree of metal contamination in this study was not more serious than that in Danube River (Europa), Rimac River (Peru), Tees River (UK), Shing Mun River (Hong Kong), and South Platte River (USA), but much worse than that of Almendares River (Cuba), Gomti River (India), Nile River (Egypt), and Yangtze River (China).

Table 3.3. Maximum concentrations of Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb in sediment of the To Lich River, Hanoi and other selected rivers around the world

Location	**Maximum concentrations (mg kg^{-1})**								**References**
	Cr	*Mn*	*Ni*	*Cu*	*Zn*	*As*	*Cd*	*Pb*	
To Lich River, Hanoi	850.6	1,649.9	206.7	210.4	1,502.0	824.5	105.2	155.5	This study
Danube River, Europa	556.5	1,655.0	173.3	8,088.0	2,010.0	388.0	32.9	541.8	Woitke et al. (2003)
Rimac River, Peru	71.0	-	23.0	796.0	8,076.0	1,543.0	31.0	2,281.0	Mendez (2005)
Tees River, UK	-	5,240.0	-	76.9	1,920.0	-	6.0	6,880.0	Hudson-Edwards et al. (1997)
Shing Mun River, Hong Kong	66.0	-	-	1,660.0	2,200.0	-	47.0	345.0	Sin et al. (2001)
South Platte River, USA	71.0	6,700.0	-	480.0	3,700.0	31.0	22.0	270.0	Heiny and Tate (1997)
Almendares River, Cuba	23.4	-	-	420.8	708.8	-	4.3	189.0	Olivares-Rieumont et al. (2005)
Gomti River, India	88.7	834.7	76.1	245.3	343.5	-	17.8	156.3	Sigh et al. (2005)
Nile River, Egypt	274.0	2,810.0	112.0	81.0	221.0	-	-	23.2	Rifaat (2005)
Yangtze River, China	205.0	-	-	129.0	1,142.0	29.9	3.4	98.0	Yang et al. (2009)

In terms of Zn concentration, 69% sediment samples exceeded maximum permissible concentration (MCC) for crops, while Cd, Ni, and Cr concentrations exceeded 30.8, 11.5, and 7.7% samples, respectively (Table 3.4). This indicated that Zn, Cd, Ni, and Cr are likely to affect crops, which are grown and regularly irrigated with mixture of water and suspended sediment of TLR. Meanwhile, 100% samples exceeded possible effect concentration (PEC) for Cu, that were 84.6, 69.2, 50.0, 34.6, 26.9 and 7.7 for Ni, Zn, Cr, As, Cd and Pb, respectively (Table 3.4). This reveals that the aquatic life is also likely to be affected, especially for organisms living close and/or in sediment. If sediment is exposed improperly, it may also affect other terrestrial organisms as well.

Table 3.4. Comparison between sediment quality guidelines (SQGs) with heavy metal concentration (mg kg^{-1}) of all sampling positions in the To Lich River, Hanoi

		Cr	Ni	Cu	Zn	As	Cd	Pb
SQGs	MCC[1]	400.0	110.0	200.0	450.0	-	3.00	300.0
	TEC[2]	43.4	22.7	31.6	121.0	9.8	0.99	35.8
	PEC[2]	111.0	48.6	31.6	459.0	33.0	4.98	128.0
This study	% of samples > MCC	7.7	11.5	3.8	69.2	-	30.8	0
	% of samples < TEC	0	0	0	0	0	15.4	3.8
	% of samples > PEC	50.0	84.6	100.0	69.2	34.6	26.9	7.7

[1] Maximum permissible concentrations of potentially toxic heavy metal for crops (Steve 1994).
[2] MacDonald et al. (2000), TEC is threshold effect concentration and PEC is probable effect concentration.

Mean PEC quotients (mPECq) were used to evaluate the toxicity for sampling positions (Table 3.1). In this study, mPECq for all nine sampling positions ranged from 0.6 to 4.0. The lowest value of mPECq (0.6, not toxic) was observed for site 9, which was located after Thanh Liet Dam and close to Nhue River. Probably, condition here was more or less the same that of Nhue River, which has been considered not as contaminated as TLR (Kikuchi et al. 2009). The highest value of mPECq (4.0, toxic) accompanied with the highest concentrations of As (824.5 mg kg^{-1}) and Pb (155.5 mg kg^{-1}) was found in S1 (Table 3.1) which was located in residential area without appearance of industrial. The discharge of water from West Lake, where many uncontrollable activities have been happening, may be responsible for such situation. In total nine sampling positions, there were four positions (S1, S4, S5, and S8) predicted to be toxic for aquatic life since mPECqs exceeded 1.5, the rest five positions were in between > not toxic and < toxic (MacDonald et al. 2000).

3.3.1.4. Cluster analysis and correlation coefficients

Cluster analysis (CA) was used to group the similar sampling positions (spatial variability) and to identify specific contamination areas (Simeonov et al. 2000; Casado-Martinez et al. 2009; Yang et al. 2009; Sundaray et al. 2011). Spatial CA rendered all nine sampling positions along the To Lich River in a dendrogram based on metal concentrations in sediment, which were grouped into three statistically significant clusters

(Fig. 3.4). Cluster 1 consisted of three sites (sites 3, 4 , and 5; Fig. 3.1), cluster 2 contained sites 2, 6, 7, 8, and 9, and there was only site 1 in cluster 3. Each cluster presents the similar characteristic features of its sites such as contamination level (Rath et al. 2009; Chung et al. 2011). Cluster 1 corresponded to moderately contaminated site, where had mix inputs of industry, hospital, and domestic wastewaters. Cluster 2 corresponded to lowest contaminated sites, even those sites (sites 6, 7, 8, and 9) are located at downstream section, where many industrial factories discharge untreated wastewater to river. Low contamination of such sites resulted from Thanh Liet Dam controlling (Fig. 3.1) which may bring all sediment to Nhue River because of high water flow rate up to 45 m^3/s, when the dam gate opens. Cluster 3 corresponded to highest contaminated site as result of discharge of wastewater from West Lake (Fig. 3.1) where was reported that there have been many uncontrollable activities carried out.

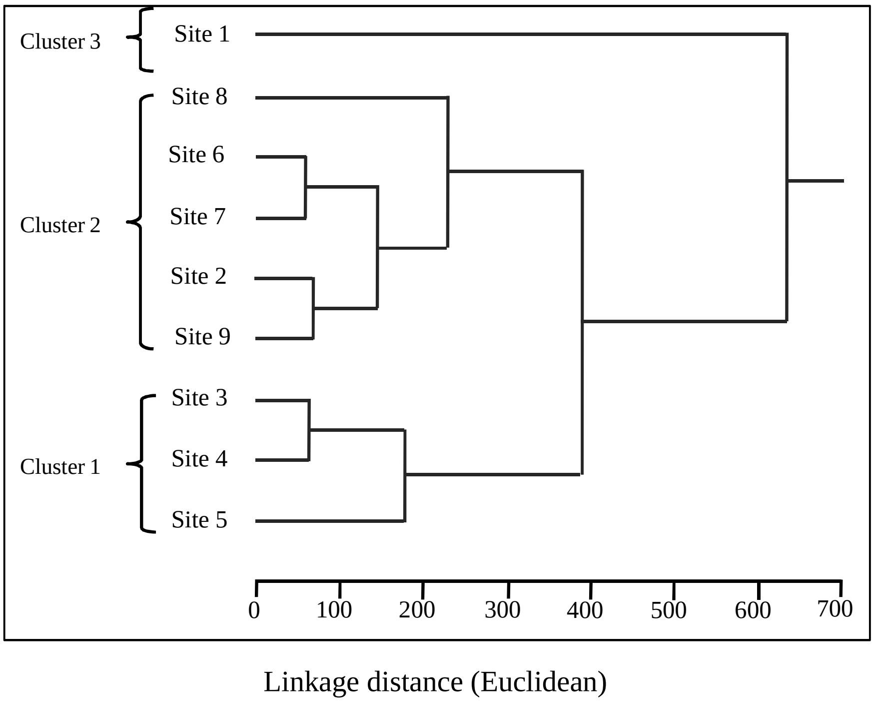


Fig. 3.4 Dendrogam showing clusters of sediment sampling positions along the To Lich River, Hanoi

There were strong positive correlations for some pairs of heavy metal in sediments; Fe-As (r = 0.99), Mn-Fe (r = 0.92), Mn-As (r = 0.91), Cu-Zn (r = 0.89), Cr-Ni (r = 0.8), Ni-Zn (r = 0.75), Cu-Pb (r = 0.72), and Cr-Zn (r = 0.71). Subramanian et al. (1987) and Caliani et al. (1997) had the same conclusion for such pairs of metal correlation for studies in Ganges and Brahmaputra River India, and Huelva Atlantic Spain, respectively. Meanwhile, strong positive relationships between TOC in water and heavy metals in sediment (Table 3.5) were also found for Mn (0.75), Pb (0.73), As (0.61) and Ni (0.60), implying that increase TOC in water leads to increase concentration of those metals in sediment. The same phenomenon was found by Facetti et al. (1998), since organic compounds have metal binding properties (Bolt and Bruggenwert 1976). In terms of pair relationships of TOC and metals in water and that in sediments (Table 3.5), there were negative relationships (increase concentration in water leads to decrease that in sediment) for Pb (-0.73), Cu (-0.63) and TOC (-0.59), and positive relationship for Mn (0.70). The same phenomenon was found for River Rhine floodplain in the Netherlands (Middelkoop et al. 2002), since discharge affects sedimentation, and then heavy metal deposition.

Table 3.5. Correlation coefficients of total organic carbon (TOC) in water and metals in sediment, and of TOC and metals in sediment with that in water of the To Lich River, Hanoi

	TOC	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
TOC in water with metals in sediment	-	0.02	0.75	0.60	0.46	0.17	0.61	0.05	0.73
TOC and metals in sediment with that in water	-0.59	0.27	0.70	-0.26	-0.63	0.35	0.20	-	-0.73

3.3.1.5. Possible sources of heavy metals of sediment profile

Generally Table 3.6 and Fig. 3.5 show possible sources of each sediment layers. For 30-60 and 60-90 cm sediment layers, they were forming the same metals in clusters and in factors, it indicated that metals in those two layers has the same possible sources as discussed in Fig.3.5. While, it was much different for 90-120 cm layer, which formed only two factors in principal component analysis. For 0-90 cm layers, As, Fe, Mn, and Pb came from mix of both anthropogenic and natural sources, while Mn, Fe, Cu, and Zn in 90-120 cm layer may come from mix sources. In the past, corresponding to 90-120 cm layer, Pb came most from anthropogenic source because of using Pb blended gasoline by old types of vehicles, which may emitted much amount of Pb. In recent years, corresponding to 0-90 cm layers the source for metal is more or less the same. This may be because of gradual increasing of the manufacturing activities of industrial zones as result of economic development processes.

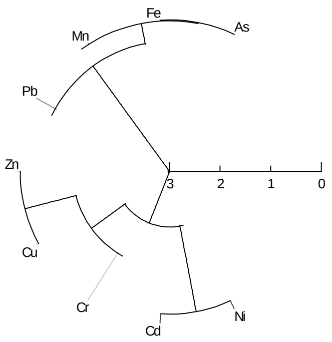
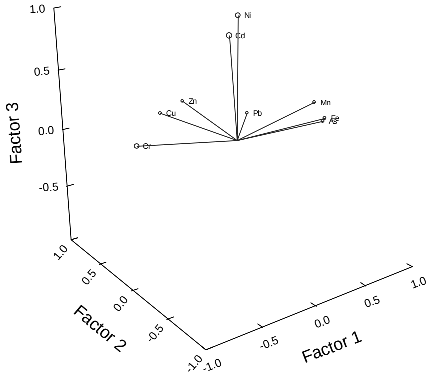
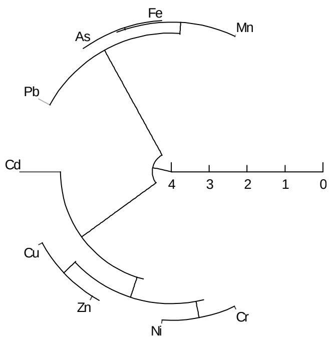
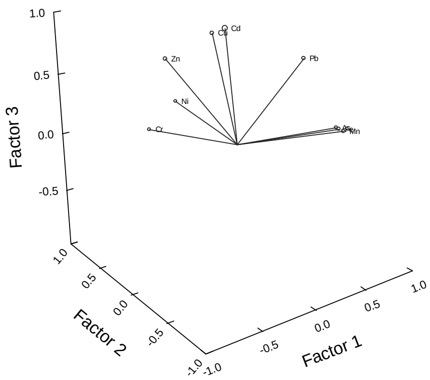
Table 3.6. Statistical results of factor analysis

a. Matrix to be factored

	Cr				Mn				Fe				Ni				Cu				Zn				As				Cd				Pb			
Sediment layer	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120	0-30	30-60	60-90	90-120
Cr	1	1	1	1																																
Mn	-	-	-	0.1	1	1	1	1																												
Fe	-	-	-	0.1	**0.9**	**0.9**	**0.9**	**0.9**	1	1	1	1																								
Ni	-	**0.9**	**0.8**	-	0.1	-	-	0.0	0.0	-	-	0.0	1	1	1	1																				
Cu	0.2	0.4	0.4	0.0	0.0	0.0	0.1	**0.9**	-	0.1	0.1	**0.9**	0.0	0.6	0.6	0.1	1	1	1	1																
Zn	0.0	**0.7**	0.6	-	0.2	-	0.0	**0.9**	0.1	-	0.0	**0.9**	0.1	**0.8**	**0.7**	0.3	**0.9**	**0.8**	**0.9**	**0.9**	1	1	1	1												
As	-	-	-	**0.7**	**0.9**	**0.9**	**0.9**	**0.7**	**0.9**	**0.9**	**0.9**	**0.8**	-	0.0	-	-	0.0	0.1	0.1	**0.7**	0.1	-	0.0	0.6	1	1	1	1								
Cd	0.1	-	-	-	-	-	-	-	-	-	-	-	**0.8**	0.0	0.2	0.5	-	0.6	0.3	-	-	0.4	0.2	-	-	-	-	-	1	1	1	1				
Pb	0.0	-	-	**0.9**	**0.7**	**0.7**	**0.7**	0.3	0.6	**0.7**	**0.8**	0.4	-	0.2	0.1	-	0.5	0.6	0.6	0.2	0.5	0.3	0.5	0.1	**0.7**	**0.7**	**0.8**	**0.8**	-	0.3	0.1	-	1	1	1	1

Table 3.6 (Continued)

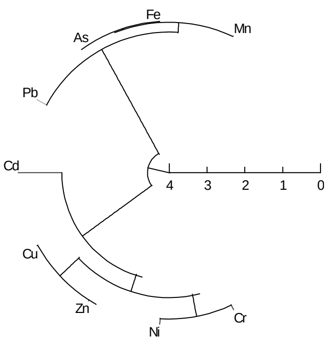
b. Rotated loading matrix (VARIMAX Gamma = 1.000)												
	Sediment layer											
	0-30			30-60			60-90			90-120		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3
Cr	**-0.70**	0.33	0.00	-0.21	**0.96**	-0.13	-0.35	**0.83**	-0.35	0.00	**1.00**	0
Mn	**0.97**	0.21	0.03	**0.97**	-0.14	-0.07	**0.97**	-0.10	-0.12	**0.99**	0.14	0
Fe	**0.98**	0.09	-0.07	**0.99**	-0.07	-0.08	**0.98**	-0.07	-0.09	**0.98**	0.18	0
Ni	0.07	0.08	**0.97**	0.06	**0.98**	0.05	-0.18	**0.92**	0.03	0.19	**-0.98**	0
Cu	-0.10	**0.97**	-0.05	0.22	0.65	**0.70**	0.30	**0.83**	0.37	**1.00**	0.01	0
Zn	0.10	**0.94**	0.01	-0.09	**0.86**	0.49	0.19	**0.93**	0.22	**0.99**	-0.11	0
As	**0.98**	0.11	-0.10	**0.98**	-0.05	-0.07	**0.98**	-0.05	-0.08	**0.70**	**0.70**	0
Cd	-0.19	-0.17	**0.92**	-0.13	-0.03	**0.97**	-0.15	0.11	**0.94**	-0.69	**-0.72**	0
Pb	**0.59**	**0.67**	-0.12	**0.84**	0.22	0.48	**0.88**	0.33	0.30	0.23	**0.97**	0
Eigenvalues	3.7	2.5	1.8	3.7	3.1	1.9	3.9	3.2	1.3	5.0	3.9	0
% total variance	42.2	27.8	20.4	41.4	34.8	21.6	44.1	36.2	14.7	55.5	44.4	0

Sediment layer	Cluster analysis (Dendrogram using Ward’s method)	Principle component analysis (Factor loadings plot)
0-30	 Linkage distance (Pearson) There were two clusters forming in 0-30 cm layer sediment. Cluster 1 was from Pb, Mn, Fe, and As with quite high correlation coefficients of metal pairs (Table 3.6). In cluster 2, two sub-clusters were formed. The first one was from Ni and Cd, and the second one was from Cr, Cu, and Zn. The pair metal correlation coefficients in cluster 2 were rather weaker than that in cluster 1 (Table 3.6).	 Three factors were formed in 0-30 cm sediment layer. Factor 1 contributed 42% variance containing Mn, Fe, As, Cr, and Pb. Those metals corresponded to mix source of both natural source for Mn, Fe, and As and anthropogenic source for Cr (mechanical) and Pb (vehicle emission). Factor 2 contributed 27% variance consisting of Cu, Zn and Pb, those from anthropogenic source of fertilizing and fertilizer manufacturing for Cu and Zn and vehicle emission for Pb. Factor 3 contributed 20% variance including Ni and Cd from anthropogenic source.
30-60	 Linkage distance (Pearson)	

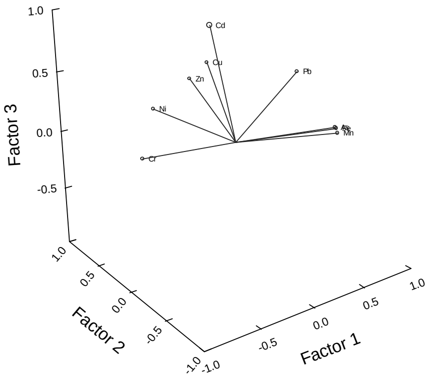
There were two clusters forming for all concerned metals in 30-60 cm sediment layer. Cluster 1 was formed by As, Fe, Mn and Pb, in which those three former metals had high correlation coefficients (Table 3.6). High correlation coefficients were found for pairs of Ni-Cr and Zn-Cu, those four metals combined with Cd to form cluster 2 in 30-60 cm sediment layer.

Factor 1 contributed 41% of variance including 4 metals; Mn, Fe, As, and Pb (Table 3.6), which may originate from mix source of both anthropogenic and nature. Factor 2 contributed 34% variance containing Cr, Ni and Zn, and factor 3 contributed 21% variance containing Cu and Cd. Those five metals in factor 2 and 3 mainly came from anthropogenic sources such as mechanical industrial, fertilizer manufacturing, leathering painting, etc.

60-90



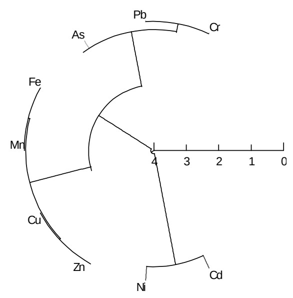
Linkage distance (Pearson)



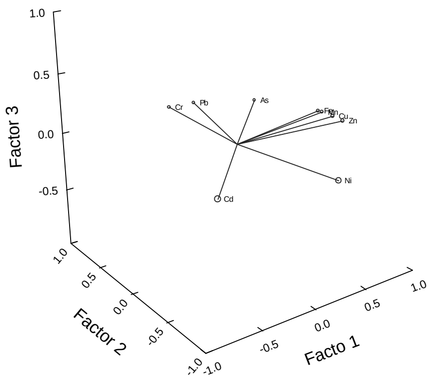
The 60-90 cm sediment layer showed the same result of cluster analysis as in 30-60 cm, including two clusters of the same metals in each cluster with more or less the same correlation coefficients for pair of corresponding metals (Table 3.6)

Corresponding to the same metals in clusters, there were also the same metals in factor analysis of 60-90 cm and that of 30-60 cm. This indicated that the possible sources of metals of those two sediment layers were more or less the same. Probably, the manufacturing activities of five industrial zones located in inner Hanoi city were the same at the time corresponding to 30-60 and 60-90 cm sediment layer, probably 8-10 years ago.

90-120



Linkage distance (Pearson)



There were two main clusters formed for nine concerned metals in 90-120 cm sediment layers. Cluster 1 was formed by seven metals, in which they formed two sub-clusters. The first sub-cluster was formed by As, Pb, and Cr with quite high correlation coefficient between metal pair (Table 3.6). The second sub-cluster was formed by Fe, Mn, Cu, and Zn with correlation coefficients of metal pair > 0.95. Meanwhile, Ni and Cd formed cluster 2 separately, which had quite low correlation coefficient of 0.57.

Unlike other sediment layers, factor analysis in 90-120 cm sediment layer indicated that metals formed only two factors. Factor 1 contributed 56% variance containing Mn, Fe, Cu and Zn, those metals may respond to the mix source of both anthropogenic and nature as Mn and Fe mainly from nature and Cu and Zn mainly from industrial like fertilizing and fertilizer manufacturing, and mechanical industrial. Factor 2 contributed 44% variance including Cr, Ni, As, Pb and Cr, which mainly came from industrial sources such as painting, leathering, mechanical and vehicle emission.

Fig. 3.5 Factor loadings plot and Dendrogram of different sediment layer

3.3.2. Surface water

3.3.2.1. Chemical properties and comparison with water quality guidelines

The results of pH, total organic carbon (TOC), and metal concentrations in water are shown in Table 3.7. There was not much difference among sampling positions in term of pH, ranging from 7.2 to 7.5. The difference became clearer for TOC, ranging from 4.3 to 10.7 with the mean of 7.7 mg L^{-1}. The highest TOC belonged to S1, where flow rate was quite low and high TOC seemed to be resulted from household wastewater discharge. While, the lowest TOC was at S9, which may be attributed to high water flow rate from opening Thanh Liet Dam. TOC at other sampling positions in the mid-section of the river was more or less equal. The concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb at all nine sampling positions were lower than permitted concentrations for irrigation water (WHO 2006) and acute value for protecting aquatic life (USEPA 2006), meanwhile concentration of Mn at seven of nine sampling positions except S2 and S6 exceeded irrigation water standard (WHO 2006). Mn concentration was much different depending on sampling positions, lowest concentration (83.7 µg L^{-1}) at S2 and highest (430.6 µg L^{-1}) at S1. Again, uncontrollable activities in West Lake may be responsible for such high concentration of Mn in S1 (Fig. 3.1).

Table 3.7. pH value, concentration of TOC (mg L^{-1}) and heavy metals (µg L^{-1}) in water of the To Lich River, Hanoi

Sampling position	**pH**	**TOC**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
S1	7.5	10.7	5	430.6	5	4	93	51.7	0.2	7
S2	7.2	4.7	2	83.7	5	5	58	47.3	< 0.2	8
S3	7.3	8.3	2	400.8	5	4	40	76.2	< 0.2	7
S4	7.2	7.7	2	230.7	8	3	36	13.1	< 0.2	6
S5	7.3	8.8	5	211.4	8	3	93	41.4	< 0.2	7
S6	7.3	8.1	5	188.7	9	7	60	38.2	< 0.2	8
S7	7.2	7.8	2	200.9	7	4	28	28.1	< 0.2	10
S8	7.2	8.5	3	211.4	6	3	42	36.2	< 0.2	8
S9	7.3	4.3	2	201.7	13	7	52	32.4	< 0.2	11
Mean ±SD	7.3 ±0.1	7.7 ±2.0	3.1 ±1.5	240.0 ±108.4	7.3 ±2.6	4.4 ±1.6	55.8 ±23.5	40.5 ±17.5	< 0.2	8.0 ±1.6
WHO[1]	6.5-8		100	200	200	200	2,000	100	10	5,000
USEPA[2]	-	-	-	-	470	13	120	340	2	-

[1] Irrigation water standard (WHO, 2006).
[2] Acute value for protection of freshwater aquatic life (USEPA 2006).

3.3.2.2. Cluster analysis and correlation coefficients

Cluster analysis (CA) grouped nine sampling positions into three clusters based on similarity between sampling sites in regards of heavy metal concentration in water (Fig. 3.6). Cluster 1, which consisted of sites 1 and 3, mainly had domestic inputs. This cluster characterized by the highest concentration of Mn and As (Table 3.1), corresponded to highest contaminated site. Cluster 2 contained six sites (sites 4, 5, 6, 7, 8, and 9) from midstream to downstream corresponded to moderately contaminated site, where several manufacturing plants are located. Site 2 alone formed cluster 3 corresponded to lowest contaminated site.

The dissimilarity in clustering metal contaminated degrees between sediment and water was observed for sites 3, 6, 7, 8, and 9 (Fig. 3.4 and Fig. 3.6). This indicated the complexity of contamination in sediment and water, since many factors affect metal concentration in water and metal accumulation in sediment such as the proximity of river contamination, river activity (flow rate) and the intensity of geomorphic activity of the river basin (Martin 2000).

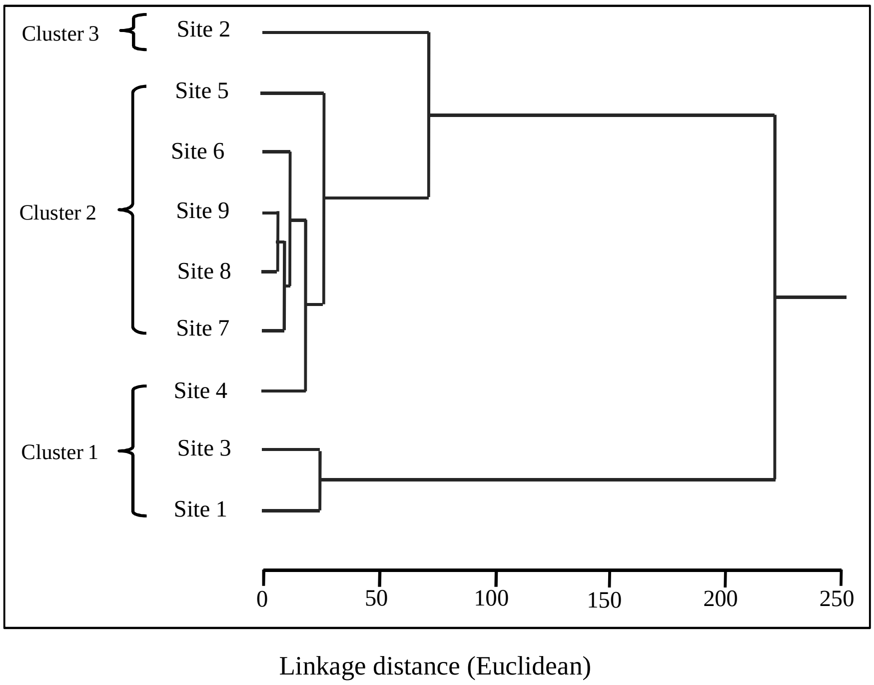


Fig. 3.6 Dendrogam showing clusters of water sampling positions along the To Lich River, Hanoi

There were no inter-element correlations in water, except pair of Zn-Cr (r = 0.66). While, positive linear of inter-element relationship was found for Cu, Pb, Zn, Cr, Ni, As, and Cd (Subramanian et al. 1987; Caliani, et al. 1997; Bastidas 1999). The heavy metals discharged to water body in such studies were mostly from natural sources (e.g. precipitation, parent material decomposition) without or little industrial wastewater, which is different from the present study area. This may be concluded that manufacturing plants discharge various heavy metals to the To Lich River, which were not proportional each other.

3.3.3. Accumulation coefficient

Accumulation coefficients (Dojlido and Taboryska 1991) were calculated as quotient of the heavy metal concentrations in sediment and that in water. The accumulation coefficient in the To Lich River (Table 3.8) ranged from 2,609 (Mn) to 57,328 (Cr), following the order of Cr > Cu > Ni > Zn > Pb > As > Mn. This may imply the long accumulation history of heavy metal in this river.

Table 3.8. Accumulation coefficients of heavy metals in the To Lich River, Hanoi

	Cr	**Mn**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Mean in water (mg L^{-1})	0.003	0.240	0.007	0.004	0.056	0.041	na	0.008
Mean in sediment (mg kg^{-1})	171.985	625.649	79.435	108.366	598.129	127.916	8.048	83.461
Accumulation coefficient	57,328.4	2,606.9	11,347.9	27,091.6	10,680.9	3,119.9	-	10,432.6

Accumulation coefficient equals ratio of mean concentration in sediment to that in water.
na data not available.

Accumulation coefficients of Cr, Cu, Zn, and Pb in present study were much higher than that in Wloclawek reservoir (Dojlido and Taboryska 1991), even concentrations of those metals in water were much lower and water flow rate was higher than that of the reservoir. This again indicated that accumulation of heavy metal in sediment is affected by many factors, beside metal concentration in water and flow rate, such as how they can associate with others and re-suspend to release to water, etc. (Martin 2000).

3.4. CONCLUSIONS

In the present study, water and sediment analysis was carried out for assessment of heavy metal pollution in To Lich River (TLR), inner Hanoi city. The results indicated that concentrations of most heavy metals in water, except Mn, were lower than irrigation water limit and acute value for protecting aquatic life. Geochemical analysis showed significant heavy metal concentration in sediments suggesting the anthropogenic impacts on TLR. The Geo-accumulation index and Enrichment factor of Pb, Zn, As, and Cd showed that a considerable number of sediment samples were at moderate to extreme pollution, whereas Mn and Fe were generally within the background levels. Heavy metal concentration of TLR is at the middle level in comparison with the findings from other rivers around the world. With respect to sediment quality guidelines, sediments at all sites exceeded maximum permissible concentrations of potentially toxic heavy metal for crops and were considered to be harmful for aquatic life. According to mean probable effect concentration quotients, sediments of sites 1, 4, 5, and 8 are predicted to be toxic to sediment-dwelling organisms. Cluster analysis suggested that the sediment from TLR can be significantly distinguished into three groups in terms of contamination degrees. Accumulation ability of heavy metals in sediment was in order of Cr > Cu > Ni > Zn > Pb > As > Mn based on accumulation coefficient.

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CHAPTER 4. DOES EMBANKMENT IMPROVE QUALITY OF A RIVER? A CASE STUDY IN TO LICH RIVER INNER CITY HANOI, WITH SPECIAL REFERENCE TO HEAVY METALS

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ABSTRACT

To Lich River (TLR) system receives wastewaters from a population of nearly two million people and 100 manufactories of five industrial zones in inner city Hanoi, Vietnam. To improve quality of TLR, the embankment was carried out in 1998 and finished in 2002, resulted in width of 20 - 45 m, depth of 2 - 4 m, and maximum water flow capacity of 30 m^3/s. Water and sediment quality indices based on heavy metal concentrations were used to evaluate current river environment compared to that of pre-embankment. Mass balance model was employed to estimate total metal loads for specific river reaches, which corresponds to various types of wastewater discharged along the river. The results indicated that currently there is about 284,000 m^3 sediment accumulated in TLR bed, which is under high contamination of Cr, Mn, Fe, Ni Cu, Zn, As, Cd, and Pb with a total of 7,347 tons of all concerned metals. Domestic-discharged river reaches received much lower metal loads, roughly 8-28% compared to river reaches of both domestic and industrial inputs. Total load of all nine concerned metals at the end of TLR is 161.7 kg/day, which is finally discharged to Nhue River at South Hanoi. Water quality was improved much right after finishing embankment, then it gradually deteriorated. Meanwhile, sediment quality became even much worse after embankment. Relative river quality index as equal weight for both water and sediment quality indices indicated that quality of TLR was not much improved after the embankment. It even became worse due to the urbanization in recent years.

Keywords: Industrial discharge, Mass balance, Metal load, River quality index, Sediment accumulation.

4.1. INTRODUCTION

The economic, social, and environmental importance of water resource cannot be overstated. Water is a vital resource for healthy living conditions and sound ecosystems. Among the relevant issues that can be analyzed, water quality is quite significant (Schiff and Winters 2002). Water body of polluted rivers, especially in densely populated cities, is usually blamed as a critical source of waterborne diseases and others. It is estimated that approximately one-quarter of the global disease burden and more than one-third of the burden among children are due to modifiable environmental factors (Saracci and Vineis 2007; Pruss-Ustun and Corvalan 2007, 2006). Materials, which are widely used in industries for their physical qualities, have proved carcinogenic, mutagenic and/or teratogenic in human (Rothman and Greenland 1998; Suser 1991). Those materials are much responsible for reduce of environmental quality, ecosystem degradation, etc. Residual of those materials from industries, if managed improperly, is finally discharged to environment especially water bodies and accumulated in sediment.

Water bodies in a city are usually serving as discharging wastewaters. The health of a river is much depending on quality of discharged waters to its body. In being urbanized cities of developing countries, wastewater treatment is not much taken care leading to over pollution of water bodies. Pollution is facilitated in several respects in urban basins. First, un- and/or partially treated wastewater from both industry and municipality is discharged directly. Second, construction generates a number of pollutants that easily adsorb or dissolve in runoff. Third, high background pollution loads often accumulate in urban areas between rainy events, mostly from structural deterioration and improper disposals of solid waste of industry and municipality, and others. Many of those pollutants easily adsorb to particles suspended in runoff from construction sites as well (Schueler 1987). The pollution loads often adversely affect water and sediment quality, and biological communities (Crawford and Lenat 1989, Mason 1981).

Sedimentation is a natural process and represents a fundamental part of ecosystem functioning that is essential to the health of rivers and water bodies (Guy 1972). Many human activities such as manufacturing, construction, transportation as a manner of moving dirty, dramatically increase the rate of erosion, resulting in larger than normal sediment deposits in inner city rivers with various organic and heavy metal contaminants. Sediment loads from construction can be 10 - 20 times greater than cultivated lands (Owen 1975), and its delivery ratios of 0.5 - 1.0 are often reported for urban basins

(Simmons 1987, Novotny and Chesters 1989). Those sediment loads often exceed the natural assimilative and equilibrating capacities of the receiving water systems. The contaminants of most concern are metals, polyaromatic hydrocarbons, polychlorinated biphenyls, and mineral oil. Therefore, disposal of polluted dredged sediments on land may lead to certain risks. Dredging is necessary to increase water flow rate, but also for remediation, whereas the risk for the environment and health might be high. Meanwhile, dredging of contaminated sediments faces problem of treatment and disposal of these contaminated sediments (Bortone et al. 2004). Currently, contaminated dredged sediments are often not valorisable due to their high content in contaminants and their consequent hazardous properties. Organics can be destroyed in place, whereas metals are immutable and relatively immobile. In addition, it is generally admitted that treatment and reuse of heavily contaminated dredged sediments is not a cost-effective alternative to confined disposal.

This study aims at (1) evaluating contamination level of sediment and water, and quality of To Lich River (TLR) after 9 years embankment, (2) estimating total load of total organic carbon and heavy metals entered and accumulated in sediment in specific river reaches corresponding to its wastewater sources, and (3) estimating daily discharge of total organic carbon and heavy metals at the end of TLR.

4.2. MATERIALS AND METHODS

4.2.1. Study site

There are four main rivers forming To Lich River (TLR) system, which receives wastewaters from inner city of Hanoi and covers a basin area of 77.5 km^2 (Nguyen 2005). To Lich is the biggest river receiving wastewaters from western part of Hanoi, while Kim Nguu, Set and Lu are three smaller ones receiving wastewaters from eastern part before discharging to TLR in downstream (Fig. 4.1). TLR originates from West Lake in North Hanoi, receiving mainly domestic wastewater in upstream and mix of domestic and industrial wastewater in downstream before joining Nhue River in South Hanoi through Thanh Liet Dam (Fig. 4.1). The construction of embankment was completed in 2002, covering most of river reaches. The un-embanked upstream reach, which has a narrow width of 1 - 4 m, is subjected to convert into a closed sewer. Currently, the embanked river reaches have a width of 20 - 45 m and depth of 2 - 4 m, and a maximum flow capacity of 30 m^3/s. There are 239 point sources, including both pipe and box culverts along TLR (Nguyen 2005). Non-point sources are also available, such as illegal dumping practices and urban storm water runoff. In dry season, water released from West Lake is limited because of low water level. The input flow then is mainly wastewaters from households and industry with high contaminants (HENRD 2009).

There are five industrial zones located in TLR system basin, in which no suitable wastewater treatment systems are available (Nguyen 2005). Thuong Dinh industrial zone consists of 30 manufacturing plants, which have been directly discharging un- and/or partially treated wastewater to downstream reach of TLR. Those plants include: fourteen of mechanical industry, four of textile industry, three of leather industry, two of chemical industry (rubber and soap), two of ceramic industry, one of tobacco industry, one of paper industry, and three others. Other four industrial zones, including 69 plants of all types of industries, discharge wastewaters to Lu, Set, and Kim Nguu rivers, before entering TLR in downstream (Fig. 4.1).

Thanh Liet Dam was built at 0.5 km from downstream to control water flow direction of TLR (Fig. 4.1). The dam is closed when water level of TLR is lower than that of Nhue River and/or water of TLR is too polluted, which may affect the agricultural production at downstream of Nhue River. In such case, water runs to Yen So Lake through downstream reach of Kim Nguu River and then it is pumped to Red river.

4.2.2. Sample collection

Surface water and sediment of 0-30, 30-60, 60-90, and 90-120 cm depths were collected at five sites along the river (Fig. 4.1). The first and second sampling sites were located in embanked river reach, receiving most domestic and hospital wastewater. The third sampling site was located right before discharge of Thuong Dinh industrial zone. The fourth and fifth sampling sites were located in un-embanked river reach, after confluence with Lu and Kim Nguu rivers, respectively. All samples were collected in dry season in March 4-5, 2011 (no rainy days).

Water samples were collected in pre-cleaned polypropylene bottles and preserved at $4^{o}C$ in refrigerator until analysis. For heavy metal determination, the water samples were acidified with conc. HNO_3 to pH < 2. The pH of water was measured in-situ using a portable pH meter. Meanwhile, sediment samples were taken from river bed using a self-made sediment sampler and placed into polyethylene bottles.

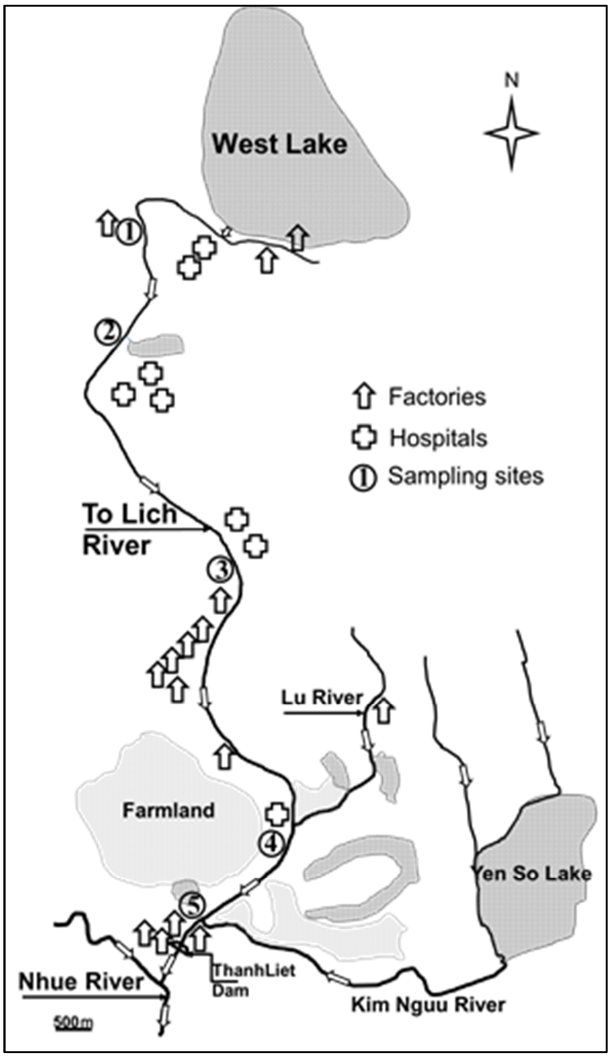

Fig. 4.1 Map of study area showing sampling sites

4.2.3. Chemical analysis

Total organic carbon (TOC) contents in water and sediment were analyzed using a TOC analyzer (TOC-5000A, Shimadzu). For heavy metal analysis, sediment samples were air-dried at room temperature and passed through 1 mm stainless steel sieve to remove big particles. Then the samples were heated in an oven at 60^{o}C until constant weight, powdered and homogenized. For microwave-assisted acid digestion procedure, roughly 50 mg dry homogenized sediment was weighed into a vessel and successively digested with 10 mL of conc. HNO_3 in a microwave digestion system (USEPA 2007**).** After cooling, the digest was transferred into a plastic volumetric flask and adjusted to 50 mL volume with Mili-Q water. The sample was finally filtered through a membrane filter (0.45 µm pore size). Concentrations of heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and

Pb) in water and acid-digested sediment samples were determined using an inductively coupled plasma-mass spectrometry (ICP-MS).

Standard operating procedures, calibration with standards, and analysis of reagent blanks, and analysis of replicates were used to guarantee the quality of analytical data. Analysis for all samples was carried out in triplicate to get the mean as final data.

4.2.4. General characteristics of river

Water flow rate (Q; m^3/s) at each sampling site was calculated as $Q = V * A_w$, where V is water velocity (m/s) and A_w is cross-section of water body (m^2). V was measured using FP101-FP201 Global Flow Probe. At each sampling site, three positions across the river (one in the center, one in each site with distance of 3 m from river banks) were measured for V to get average value. Tape was used to measure width of water surface across river, while height stick was used for water and sediment depths (Fig. 4.2). The sediment depth at each sampling site was just the depth of deepest sediment layer collected (Table 4.1). Slope of river bank was measured at each sampling site in degree to identify cross-sectional area of water and sediment bodies (Fig. 4.2).

Area of water cross-section (A_w in m^2) at each sampling site was calculated as following equation:

A_w=((W-2WD*tan(S))+W) * WD/2

=(2W-2WD*tan(S))*WD/2

=(W-WD*tan(S))*WD

=W*WD-WD^2*tan(S) (4.1)

where, W is width of water surface in meter, WD is water depth in meter, S is slope of river bank in degree.

Area of sediment cross-section (A_s in m^2) at each sampling site was calculated following Eq. 4. 2.

A_s={((W-2WD*tan(S))-2SD*tn(S))+(W-2WD*tan(S))}*SD/2

={W-2WD*tan(S)-SD*tan(S)}*SD

={W-tan(S)*(2WD+SD)}*SD

=SD*W-tan(S)*(2WD*SD+SD^2)　　　　(4.2)

where SD is sediment depth in meter.

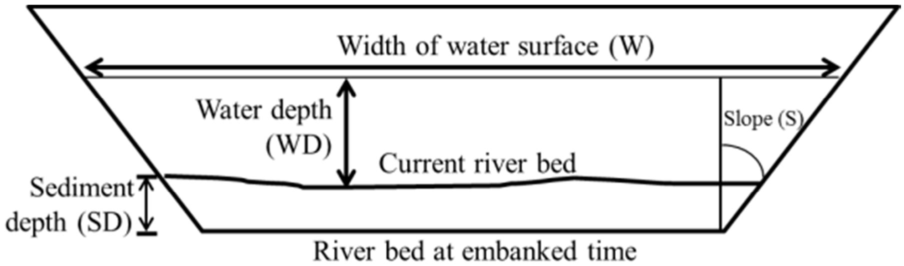

Fig. 4.2 Vertical cross section of To Lich River

4.2.5. Loading of heavy metals

Chemical mass balance model was introduced by Dolan and Shaarawi (1989) to estimate chemical load in a river reach following Eq. 4. 3.

$$Q_d C_d - Q_u C_u = \sum_{i=1}^{n} L_i \qquad (4.3)$$

where, Q_d and Q_u are downstream and upstream flows, C_d and C_u are downstream and upstream concentrations, and $\sum_{i=1}^{n} L_i$ is sum of all individual loadings to river reach. In fact, river contaminants undergo significant volatilization and/or degradation, therefore to improve the accuracy Eq. 4. 3 was modified by Jha et al. (2007) as

$$Q_d C_d - Q_u C_u e^{-kt} = \sum_{i=1}^{n} L_i \qquad (4.4)$$

where, k is coefficient of attenuation rate (day^{-1}), t is travel time (day). $Q_d C_d$ is total load in downstream and/or at the end of river reach.

4.2.6. River quality index

Water quality index has been widely used to evaluate the quality/pollution levels of rivers (Liou et al. 2004; Parparov et al. 2006; Bordalo et al. 2006; Banerjee and Srivastava 2009). In this study, we extend this knowledge to evaluate both water and sediment quality as a base for river quality assessment. In order to evaluate the improvement of river, a water quality index (WQI) and a sediment quality index (SQI) were developed based on seven parameters modeled (Cr, Mn, Ni, Cu, Zn, As and Pb for water, and Cr, Ni, Cu, Zn and Pb for sediment).

The WQI and SQI were derived as the following manners:

$$\mathrm{Index}_{\mathrm{water}_{\mathrm{metal}_i}} = \frac{\text{Concentration in water}_{\mathrm{metal}_{i\ \text{in year A}}}}{\text{Concentration in water}_{\mathrm{metal}_{i\ \text{in year B}}}}$$

$$\mathrm{WQI} \quad = \quad (\sum_{i=1}^{7} \mathrm{Index}_{\mathrm{water}_{\mathrm{metal}_i}})/7$$

where, $\mathrm{Index}_{\mathrm{water}_{\mathrm{metal}_i}}$ is quality index of metal i in water, $\text{Concentration in water}_{\mathrm{metal}_{i\ \text{in year A}}}$ is concentration in water of metal i in year A, and $\text{Concentration in water}_{\mathrm{metal}_{i\ \text{in year B}}}$ is concentration in water of metal i in year B (A > B).

$$\mathrm{Index}_{\mathrm{sediment}_{\mathrm{metal}_i}} = \frac{\text{Concentration in sediment}_{\mathrm{metal}_{i\ \text{in year A}}}}{\text{Concentration in sediment}_{\mathrm{metal}_{i\ \text{in year B}}}}$$

$$\mathrm{SQI} \quad = \quad (\sum_{i=1}^{5} \mathrm{Index}_{\mathrm{sediment}_{\mathrm{metal}_i}})/5$$

where, $\mathrm{Index}_{\mathrm{sediment}_{\mathrm{metal}_i}}$ is quality index of metal i in sediment, $\text{Concentration in sediment}_{\mathrm{metal}_{i\ \text{in year A}}}$ and $\text{Concentration in sediment}_{\mathrm{metal}_{i\ \text{in year B}}}$ are concentrations in sediment of metal i in year A and B, respectively (A > B).

Subsequently, a simple relative river quality index (RQI) was derived giving equal weight for both WQI and SQI:

$$\mathrm{RQI} = (\mathrm{WQI} + \mathrm{SQI})/2$$

where, WQI, SQI, and/or RQI equals 1 there is no improvement for water, sediment and/or river, while it is improved if the values are < 1, and becomes worse if the values are > 1.

4.3. RESULTS

4.3.1. General characteristics of To Lich River

The water velocity gradually increases from up to downstream as 0.015 m/s at S1 to 0.039 at S2, 0.049 at S3, 0.117 at S4, and 0.131 m/s at S5 before discharging to Nhue River (Table 4.1). Corresponding to water velocity is water flow rate, which also increases toward downstream as result of various wastewater inputs along TLR (Table 4.1, Fig. 4.3a). The flow rate at S5 right after confluence with Kim Nguu River was 6.68 m^3/s, nearly doubled that (3.53 m^3/s) at S4 located after confluence with Lu River. The same pattern was found between S3 and S4. Those indicated the high water flow rate from both Lu and Kim Nguu to TLR.

Table 4.1. General characteristics of specific reaches of To Lich River

Sampling site	**S1**	**S2**	**S3**	**S4**	**S5**
Distance from upstream (km)	3.1	5.1	9.1	13.8	15.5
Water depth (m)	0.75	0.84	0.98	1.05	1.34
Area of water cross section (m^2)	11.91	14.50	23.83	30.25	50.97
Water velocity (m/s)	0.015	0.039	0.049	0.117	0.131
Flow rate (m^3/s)[1]	0.18	0.57	1.16	3.53	6.68
Total travel time in a specific reach (days)[2]		0.85	1.05	0.66	0.18
Sediment depth (m)	1.2	1.2	1.2	0.9	0.6
Area of sediment cross section (m^2)	16.16	18.00	26.57	23.60	21.03
Mean sediment cross sectional area (m^2) for a specific reach[3]		17.08	22.29	25.08	22.31
Total sediment volume in a specific reach (m^3)[4]		34,161	89,139	117,888	42,395
Average sediment density in a specific reach (kg/m^3)[5]		1,053	1,195	1,242	1,357
Estimated cost required for treating sediment (average cost[6] of 36 USD/m^3)		1,229,784	3,209,020	4,243,957	1,526,227

[1] equals to water velocity multiplying area of water cross section.
[2] equals to ratio of length (m) to mean of water velocity (m/s) at first and last points of a specific river reach.
[3] equals to mean of first and last sediment cross sectional area of a specific river reach.
[4] equals to length of river reach multiplying mean sediment cross section.
[5] testing dry weight of known volume of sediment.
[6] composite unit costs extrapolated from case studies in USA range from a low of approximately 36 USD/m^3 to over 600 USD/m^3 (Myers 2005).

Since velocity increases toward downstream, travel time of water decreases which takes 0.43 day/km between S1-S2, 0.26, 0.14 and 0.09 day/km between S2-S3, S3-S4 and S4-S5 river reaches, respectively. As a consequence, sediment also become shallower toward downstream; 1.2 m depth at S1, S2 and S3, 0.9 m at S4, and only 0.6 m at S5 (Table 4.1, Fig. 4.3b). Based on cross-sectional area of sediment body and length of each river reach, total sediment accumulated in river bed was estimated. Lowest amount of sediment of 34,161 m^3 was observed at reach between S1-S2, then 42,395 between S4-S5, 89,139 between S2-S3, and the highest of 117,888 m^3 between S3-S4. Meanwhile, sediment density increases gradually to downstream (Table 4.1).

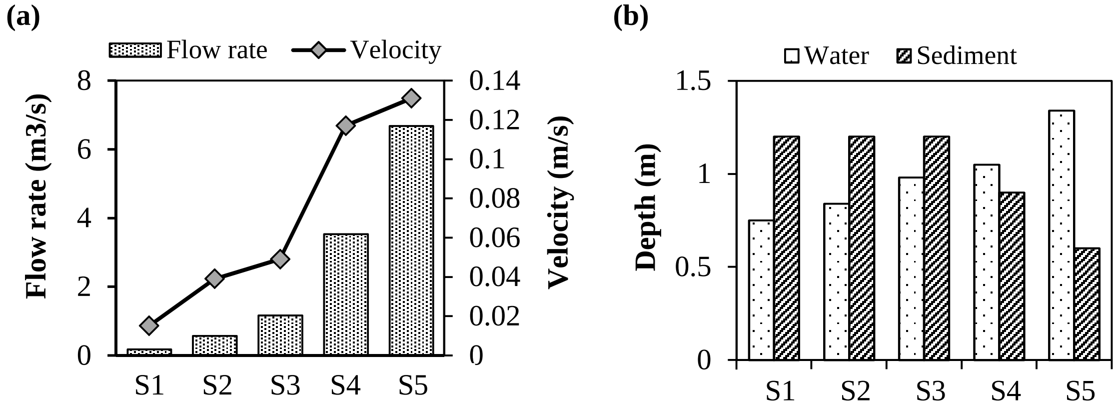

Figure 4.3 River characteristics

4.3.2. Sediment quality

High variation of total organic carbon (TOC) and heavy metal concentrations among sampling sites was found (Table 4.2). TOC content varied between 11 at S4 and 60 g/kg at S3. Meanwhile, Cr ranged from 90 at S4 to 229 mg/kg at S2; Mn ranged from 392 at S1 to 610 at S2; Fe ranged from 13,139 at S1 to 22,442 at S4; Ni ranged from 51 at S2 to 98 at S3; Cu ranged from 57 at S4 to 146 at S2; Zn ranged from 255 at S4 to 783 at S3; As ranged from 16 at S4 to 28 at S3; Cd ranged from 1.0 at S1 to 35 at S3; and Pb ranged from 58 at S4 to 92 mg/kg at S3. Comparing among heavy metals, the average concentrations in sediment increased following the order of Cd <As <Ni <Pb< Cu < Cr <Mn<Zn < Fe (Table 4.2).

Concentrations of Zn and Cd far exceeded the maximum permissible concentrations of potentially toxic heavy metal for crops after application of sewage sludge **(**Steve 1994). Comparing to Vietnamese standard, contents of most concerned heavy metals exceeded the allowable limit for both agricultural and industrial soils (Table 4.2).

Table 4.2. Mean[1] concentration (±SD) of total organic carbon (TOC; g/kg) and heavy metals (mg/kg) in sediment at specific sampling sites along To Lich River

Sampling site	**TOC**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
S1	48.3 ±7.1	229.0 ±75.3	392.0 ±57.6	13,139.5 ±3,142.7	51.4 ±6.7	103.6 ±18.0	513.4 ±73.4	21.6 ±4.2	1.0 ±0.2	75.9 ±15.7
S2	33.5 ±3.0	144.7 ±36.1	610.9 ±92.4	21,718.3 ±4820.2	77.4 ±12.1	146.8 ±12.0	770.6 ±82.6	24.7 ±3.9	2.3 ±0.3	90.4 ±10.0
S3	60.8 ±15.3	128.4 ±36.3	438.5 ±121.9	16,783.3 ±5,308.0	98.4 ±17.5	139.7 ±50.6	783.1 ±301.8	28.9 ±13.5	35.3 ±47.0	92.3 ±27.1
S4	11.7 ±7.6	90.1 ±24.4	572.0 ±53.5	22,442.8 ±2,373.4	68.7 ±21.7	57.8 ±21.8	255.2 ±137.5	16.7 ±4.0	4.0 ±4.9	58.7 ±14.2
S5	19.5 ±3.5	132.7 ±34.6	538.8 ±50.4	21,585.3 ±384.5	70.2 ±10.3	74.1 ±11.0	412.5 ±78.6	23.7 ±4.5	13.2 ±1.9	63.0 ±8.0
Mean	34.7 ±20.2	145.0 ±51.2	510.4 ±92.0	19,133.8 ±4,034.1	73.2 ±17.0	104.4 ±39.2	547.0 ±229.2	23.1 ±4.5	11.2 ±14.3	76.1 ±15.3
Sampling in 2005[2]	-	570.2	-	-	74.0	333.2	390.8	-	9.6	375.3
Sampling in 1997[3]	-	580.1	-	-	14.9	158.7	192.7	35.2	-	139.0
QCVN 03: 2008/BTNMT for agricultural soil[4]	-	-	-	-	-	50	200	12	2	70
QCVN 03: 2008/BTNMT for industrial soil[4]	-	-	-	-	-	100	300	12	10	300
MCC[5]	-	400	-	-	110	200	450	-	3	300

[1] mean of all sediment layers in each sampling site for TOC and specific heavy metal.

[2] cited from Nguyen et al. (2010).

[3] cited from HSDC (1997).

[4] QCVN 03: 2008/BTNMT - Vietnamese technical regulation on the allowable limits of heavy metals in soils.

[5] Maximum permissible concentrations of potentially toxic heavy metal for crops after application of sewage sludge (Steve 1994).

There were huge amounts of TOC and heavy metal accumulated in sediment in specific river reaches (Table 4.3). The highest amount belonged to TOC with a total of 12,745 tons in whole river sediment, followed by Fe of 6,815, Zn of 201, Mn of 179, Cr of 43, Cu of 38, Pb and Ni of 27 tons each, As of 8, and Cd of 5.4 tons.

Table 4.3. Total load of total organic carbon (TOC) and heavy metal in sediment in specific reaches of To Lich River

River reach	Unit	TOC	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
S1-S2	total (ton)	1,470.3	6.7	18.0	626.9	2.3	4.5	23.1	0.8	0.1	3.0
	kg/m^3	43.041	0.197	0.528	18.353	0.068	0.132	0.676	0.024	0.002	0.088
S2-S3	total (ton)	5,019.8	14.5	55.9	2,050.6	9.4	15.3	82.8	2.9	2.0	9.7
	kg/m^3	56.314	0.163	0.627	23.005	0.105	0.171	0.928	0.032	0.022	0.109
S3-S4	total (ton)	5,301.5	16.0	74.0	2,871.7	12.2	14.5	76.0	3.3	2.9	11.0
	kg/m^3	44.971	0.136	0.628	24.359	0.104	0.123	0.645	0.028	0.024	0.094
S4-S5	total (ton)	896.5	6.4	32.0	1,266.5	4.0	3.8	19.2	1.2	0.5	3.5
	kg/m^3	21.147	0.151	0.754	29.873	0.094	0.089	0.453	0.027	0.012	0.083
Grand total	ton	12,688.2	43.7	179.9	6,815.7	27.9	38.0	201.1	8.2	5.4	27.3

Concentration of TOC and heavy metal as mean of all layers (Table 4.2) at first and last points of specific river reach was used for calculation. Load of TOC and heavy metal equals to mean concentration multiplying total sediment amount corresponding to its density in a specific river reach (Table 4.1).

4.3.3. Water quality

There was not much variation in pH, ranging around 7.2-7.3 among sampling sites. Meanwhile, high variation was observed for total organic carbon (TOC; Table 4.4), the highest value found in S2 of 8.3 mg/L nearly doubled that in S1 (4.7 mg/L). Concentrations of Cr, Ni, Cu, and Pb were lower than 10 µg/L and not much different among all sampling sites. Meanwhile, that of Zn, As, and Mn were much higher, ranging from 36 to 60, 13-76, and 83-400 µg/L, respectively. Except Mn, all other heavy metals were still under recommended levels for irrigation water (Table 4.4).

Table 4.4. pH value, concentration of total organic carbon (TOC; mg/L) and heavy metals (μg/L) in water at specific sampling sites in To Lich River

Sampling site	pH	TOC	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
S1	7.2	4.7	2	83.7	5	5	58	47.3	< 0.2	8
S2	7.3	8.3	2	400.8	5	4	40	76.2	< 0.2	7
S3	7.2	7.7	2	230.7	8	3	36	13.1	< 0.2	6
S4	7.3	8.1	5	188.7	9	7	60	38.2	< 0.2	8
S5	7.2	7.8	2	200.9	7	4	28	28.1	< 0.2	10
Mean ±SD	7.24 ±0.05	7.32 ±1.48	2.60 ±1.34	220.96 ±114.80	6.80 ±1.79	4.60 ±1.52	44.40 ±14.03	40.58 ±23.61	-	7.80 ±1.48
Sampling in 2005[1]	7.3	21.2	8.4	114.0	6.0	4.6	31.6	5.6	-	1.9
Sampling in 1997[2]	-	-	13.0	220.0	4.0	20.0	2000.0	66.0	-	160.0
TCVN 5942-1995 B[3]	5.5-9	-	1,000	800	1,000	1,000	2,000	100	20	100
Irrigation water guidelines[4]	6.5-8	-	100	200	200	200	2,000	100	10	5,000
Freshwater[5]	-	-	1.0	8.0	0.5	3.0	15.0	0.5	-	3.0

[1] cited from Kikuchi et al. (2009).
[2] cited from HSDC (1997).
[3] Surface water quality standard in Vietnam used for the purpose other than domestic water supply including irrigation water.
[4] WHO (2006).
[5] Median values of freshwater in the world (Bowen 1979).

Using heavy metal and organic carbon concentrations of sampling sites to apply mass balance model (Equation 4), total loads of TOC and heavy metal generated to each river reach and at the end of To Lich River (TLR) before discharging to Nhue River were estimated (Table 4.5, Fig. 4.4). High variation of loads of TOC and heavy metal was found among river reaches; ranging from 338 to 2,036 kg/day for TOC, 0.07-1.35 for Cr, 3.25-58.51 for Mn, 0.18-2.04 for Ni, 0.14-1.88 for Cu, 1.25-15.19 for Zn, 3.16-10.49 for As, and from 0.24 to 3.42 kg/day for Pb. In general, river reaches of S1-S2 and S2-S3 in upstream, where received mostly domestic wastewater, had lower loads of all heavy metals and TOC compared to that of S3-S4 and S4-S5 river reaches in downstream (Table 4.5), which received various types of wastewater. TOC discharged from TLR to Nhue River reached 4,504 kg/day (Table 4.6), while that of heavy metals was much lower; 1.15 kg/day for Cr, 2.31 for Cu, 4.04 for Ni, 5.77 for Pb, 16.17 for Zn, 16.22 for As, and up to 116 kg/day for Mn.

Table 4.5. Total heavy metal and organic carbon (TOC) discharged to specific reaches of To Lich River (kg/day)

	Attenuation rate[1]	River reach			
		S1- S2	*S2- S3*	*S3- S4*	*S4- S5*
TOC	0	338	360	1,697	2,036
Cr	0.19	0.07	0.12	1.35	-
Mn	0	18.55	3.25	34.40	58.51
Ni	0.21	0.18	0.60	2.04	1.40
Cu	0.25	0.14	0.15	1.88	0.27
Zn	0.24	1.25	2.07	15.19	-
As	0.21	3.16	-	10.49	5.01
Pb	0.19	0.24	0.32	1.91	3.42

[1] cited from Ambrose et al. (1991), there are no attenuation rates for TOC and Mn available, the value of zero was used for estimation. Estimated values of Cr and Zn in S4-S5 river reach and of As in S2-S3 river reach were negative, they were excluded.

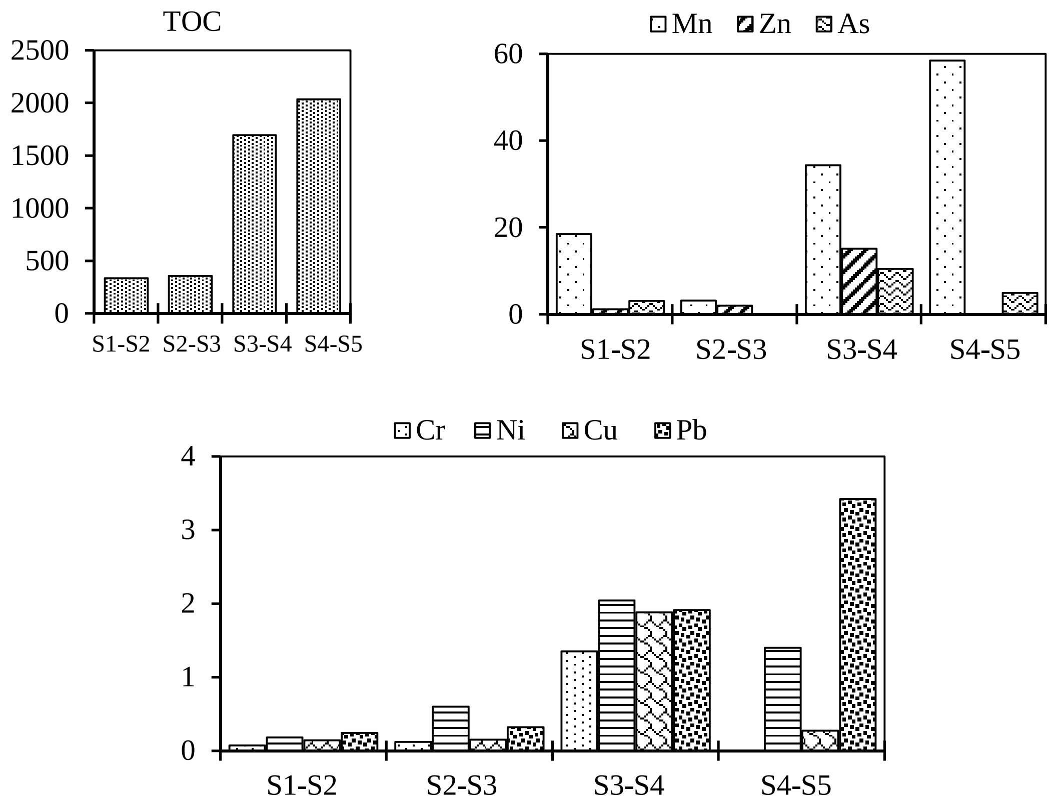

Figure 4.4 Heavy metal and total organic carbon (TOC) discharged to specific reaches (kg/day)

Based on estimated data of population, water supply per capita, and water use in industry in TLR system basin, discharge of TOC and heavy metals from To Lich to Nhue River was estimated (Table 4.6). Wastewaters volume increased year by year, from 450,922 m^3/day in 2005 to 577,399 m^3/day in 2011 and may up to 718,750 m^3/day in 2020. This was accompanied by the increase in heavy metals loaded to Nhue River; Mn of 51.41 kg/day in 2005 to 116 in 2011 and to 144.4 kg/day in 2020, As of 2.53 kg/day in 2005 to 16.22 in 2011 and to 20.20 kg/day in 2020, and other heavy metals (Table 4.6).

Table 4.6. Total load[1] of total organic carbon (TOC) and heavy metal at the end of To Lich River before discharging to Nhue River by year (kg/day)

Year	TOC	Cr	Mn	Ni	Cu	Zn	As	Pb	Water discharge (m^3/day)[2]
2005[3]	9,560	3.79	51.41	2.71	2.07	14.25	2.53	0.86	450,922
2011[4]	4,504	1.15	116.00	4.04	2.31	16.17	16.22	5.77	577,399
2020[5]	5,606	1.44	144.40	5.03	2.88	20.13	20.20	7.19	718,750

[1] equals to Q_d*C_d (Q_d and C_d are downstream discharge and concentration, respectively).
[2] at the end of To Lich River.
[3] discharge data is citied from Nguyen (2005), while TOC and heavy metal concentrations are cited from Kikuchi et al. (2009).
[4] from this study.
[5] assuming that TOC and heavy metal concentrations are the same as in this study, while discharge is based on the data of population change and change of freshwater supply per capita in TLR system basin (Nguyen 2005).

4.3.4. River quality

Table 4.7 shows values of water and sediment quality indices of To Lich River (TLR). The embankment of TLR started in 1998 and finished in 2002. To understand the efficiency of embankment on river quality, concentrations of heavy metal in water and sediment in 1997 and in 2005 were used to compare with that in the present study. Water quality was much improved in 2005 and in 2011 compared to pre-embankment as water quality index of pair of 2005-1997 was 0.43 and that of 2011-1997 was 0.55. However, quality of water in 2011 became worse than that in 2005. Conversely, sediment quality became worse after embankment indicated by index of 2.55 between 2005-1997 and of 1.84 between 2011-1997. Sediment quality in 2011 was much improved compared to that in 2005, representing by index of 0.63. Combining water and sediment quality indices indicated that river quality was not improved; it even became more polluted as values of river quality index were higher than 1 for all pairs of year comparison (Table 4.7).

Table 4.7. Water, sediment, and river quality indices of To Lich River

Pair of comparison (year-year)	Water quality index	Sediment quality index	River quality index
2011[1]-2005[2]	2.45	0.63	1.54
2005-1997	0.43	2.55	1.49
2011-1997[3]	0.55	1.84	1.19

Heavy metal concentration data: [1] from this study, [2] cited from Kikuchi et al. (2009), [3] cited from HSDC (1997).

4. 4. DISCUSSION

It is clear that water of To Lich River (TLR) should be treated prior to use on crops as the Mn concentration exceeded recommended level for irrigation (Table 4.4). Since wastewaters discharged to river reaches between S1 and S3 were mostly of domestic origin, total load of total organic carbon (TOC) and heavy metal were much lower than that in downstream reaches between S3 and S5 (Table 4.5). This may suggest the responsibility of industry for heavy metal discharges rather than of domestic practices. Higher loads of Cr, Ni, Cu, Zn, and As in river reach between S3-S4 compared to that between S4-S5 (Table 4.5) indicated that industry within catchment of Lu River, which joints TLR before sampling site S4, may generate higher amount of those metals compared to that in Kim Nguu River catchment (Fig.4.1). Load of Cr and Zn in S4-S5 and of As in S2-S3 river reaches were negative (Table 4.5), which must be always ≥ zero. This may be due to the attenuation rates of this study site are not available, then they were cited from Ambrose et al. (1991), who indicated dissolved and absorbed capacity of heavy metal as a function of suspended solid concentrations in streams around the world. It may suggests that attenuation rate of heavy metals in TLR should be higher as result of low velocity, higher concentration in water, and others.

Taking into account of TOC, which nearly upped to 4.5 tons/day (Table 4.6) discharged to Nhue River and of nutrient contents in water (Trinh, 2003), if wastewater is treated properly and reused in agriculture, it may sustain water supply, reduce input costs, and increase crop’s productivity and farm income (Rijsberman 2004). An integrated cost-benefit analysis of wastewater reuse should be conducted, after implementation of an adequate wastewater treatment system for TLR basin, which is now under consideration. Currently, agricultural products irrigated using TLR water have been ostracized by consumers because of water contamination.

Sediment of TLR cannot be directly used for any purposes neither agriculture (Steve 1994) nor industry (QCVN 03: 2008/BTNMT; Table 4.2). It must be treated following suitable guidelines for specific purpose, even treatment and reuse of heavily contaminated dredged sediments is not a cost-effective alternative to confined disposal (Bert et al. 2009), which becomes secondary source of contamination. Treatment technologies and experiences have never been put into consideration for sediment of TLR system in Hanoi, or even in the world for heavy metal contaminated sediment in general (Peng et al. 2009). This may be the barriers for environmental improvement of TLR. There was a total of 284,000 m^3 of sediment in TLR (Table 4.1), which contained high concentration of heavy metals (Table 4.2). Depending on required quality of sediment after treatment, the technologies (Foerstner and Apitz 2007) may be different leading to differences in treatment cost, ranging from 36 to 600 USD/m^3 based on composite unit cost estimation in USA (Myers 2005). Total cost estimated for treating sediment in TLR ranges from 10.2 to 170 million USD, which excludes costs for dredging, transportation, monitoring, and management of residuals. One again, after treated if it is used for agriculture much benefit will come to farmers because of high nutrient and organic carbon content in sediment. Embankment of TLR finished in 2002 (Nguyen 2005), if equalizing sedimentation deposit annually there was 30,000 m^3 of sediment accumulated in TLR bed, it may require annual cost of 1.2-19 million USD for sediment treatment.

Accumulation of Fe, Mn, Ni, Pb, As, and Cd in sediment was lowest in river reach between S1 and S2 (Table 4.3), where discharge was mostly from domestic origin (Fig. 4.1). Meanwhile, levels of Cr, Cu, Zn, and TOC was lowest in downstream river reach between S4 and S5, this may result from higher flow rate of nearly 10 times of downstream compared to upstream (Table 4.1). The highest accumulations of Mn and As were also found in downstream river reach (S4-S5; Table 4.3), even their concentrations in water were not higher than other river reaches (Table 4.4). This is explained by the higher density of sediment of S4-S5 river reach compared to others in upstream (Table 4.1) and/or those metals prefer to bind with heavier suspended particles. In general, sediment density increases toward downstream as a result of higher flow rate, which may bring higher amount of lightly suspended particles. In addition, sediment in further downstream becomes more compact which restricts re-suspended process to release heavy metals to water.

Discharge of heavy metals and TOC to Nhue River at the end of TLR in 2011 (Table 4.6) may be underestimate since it was based on water discharge of only 2 investigated days of March 4 and 5 in dry season in 2011, when there was no rain. The fact is that dirty on land surface of TLR system basin may contain much organic carbon and heavy metals as result of transportation, municipal and industrial solid waste disposals, which all will be discharged to TLR on rainy days. The same case for projected data in 2020, since concentration of heavy metals and TOC in water are predicted to be the same values in 2011 and uncertainty of population in 2020. Currently, there is no clear plan on building wastewater treatment plants for whole TLR system basin, which may lead to more serious water pollution in near future.

Water quality index (WQI) showed that quality of water was much improved after embankment (Table 4.7) as result of reducing stagnation due to improving flow rate. Because of no suitable wastewater treatment, river management strategy and/or elevated discharge of heavy metals to wastewaters from urbanization, water quality has been becoming worse indicated by increase of WQI to 2.45 between 2011 and 2005 (Table 4.7). Conversely, it was observed for quality of sediment. Sediment became more polluted after embankment, indicated by sediment quality index (SQI) of 2.55 and 1.84 for pairs of 2005-1997 and 2011-1997, respectively. The fact is that sediment was almost removed from river bed as preparation for embankment activities, the new layers of sediment were accumulated afterward. Since 2002 after completing embankment, population growth, rapid urbanization, and speed-up of manufacturing activities of industrial zones within TLR system basin led to increasing the amount and pollution level of discharges, which contained high amount of suspended particles for sedimentation process (Nguyen 2005). However comparing between 2005 and 2011, sediment quality was improved (SQI = 0.63). Probably, pre-physical wastewater treatment was paid much attention by industrial zones to remove as much big particles as possible before discharging as result of issuing environmental regulations recently. The health of a river should be considered in terms of both water and sediment bodies, hence river quality index (RQI) was derived from WQI and SQI (Table 4.7). Quality of TLR has not yet improved since embankment, it even became worse. To improve quality of a river, wastewater should be treated properly before discharging to its body. Meanwhile, the main purpose of TLR embankment was improving water flow rate and reducing solid waste disposal on river banks.

4. 5. CONCLUSIONS

This study indicated that concentration of only Mn in water of To Lich River (TLR) inner Hanoi City, Vietnam exceeds irrigation standard, meanwhile concentrations of Cu, Zn, As, and Cd in sediment exceed Vietnamese standard for both agricultural and industrial soils.

There is an amount of nearly 300,000 m^3 sediments accumulated in TLR since finishing embankment in 2002, which may cost up to 170 million USD for treatment. Even though, the technologies and experiences are still limited in study site.

After almost ten years of embankment, quality of TLR was not improved; it even became more contaminated in terms of heavy metals in both sediment and water. To improve the environmental quality of a river, embankment is not enough and just an initial stage. In the next step, wastewater should be fully treated at sources before discharging to TLR and if possible annual sediment dredging should also be implemented. This not only increases water flow rate, but also reduces re-suspended process of heavy metals from sediment.

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CHAPTER 5. GENERAL DISCUSSION AND MANAGEMENT IMPLICATIONS

5.1. General discussion

There were many cases of massive fish death in basin of Nhue River reported as results of discharge of over-polluted wastewaters from To Lich River (TLR), especially in dry season. Two possibilities of reducing pollution level of wastewater are (1) all wastewater must be treated following suitable guidelines of different using purpose such as irrigation, however it may be a long term project since building a system of wastewater treatment plant for TLR basin with recent amount of 600,000 m^3 per day is costly, (2) supplying unpolluted water from available sources to TLR, which will help reducing pollution to safety level for both aquaculture and agriculture. As mentioned in Chapter 1, Red river runs through Hanoi city with huge amount of discharge even in dry season. Currently water from Red river cannot runs naturally to TLR as result of river encroachment in upstream, dredging will resolve this problem. Meanwhile, even huge amount of discharge since water level of Red river in dry season is low which may not runs naturally to TLR, a pumping station should be established.

Annually, there is about 30,000 m^3 sediment accumulated in river bed of TLR as mentioned in Chapter 4. There are a number of sources leading to high amount of sediment as: (1) soil erosion from agricultural activities, this has been reduced much as result of reduce of agricultural land from urbanization in recent years; (2) residuals from construction activities in TLR basin, which has been much increased as increase of a number of new buildings, expansion of transportation system, etc.; (3) movement of dust to city through vehicles, since transportation system surrounding Hanoi has not much been developed. To reduce amount of sediment in TLR, the cheapest way can be done by issuing suitable regulations such as all vehicles must be washed before entering the city and other regulations for construction activities.

Even being highly urbanized in recent decades, there is still an area of agricultural land which has been directly irrigated by wastewater from TLR through pumping stations along river and such land still sustains life for a portion of citizens in inner Hanoi city. The fact is that agricultural products, especially vegetables irrigated by TLR wastewater have been ostracized by consumers. In the near future, agricultural land may be destructed as a result of urbanization; establishing irrigation system for such land becomes cost-inefficient. Therefore, only one way farmers can sustain their products is that they should not only irrigate with wastewater from TLR but also with their own clean water by suitable ratio, which ensures the quality of products acceptable by government standard and reduces input cost from using so much clean water and nutrient/fertilizer that is much available in wastewater.

After embankment in 2002, river banks of TLR have become playgrounds for many citizens living along and surrounding areas, even it is reported that bad odor is coming from water body. People may not directly contact with water body, however many water-borne diseases are originated such as diarrhea from *Escherichia coli* bacteria, which much affect human health. *E. coli* bacteria usually transfers to human through food chain by consuming raw material such as vegetables which contains *E. coli.* Those can be avoided by not eating raw vegetables irrigated by TLR water and/or vegetables should be washed in a clean manner to remove as much *E. coli* as possible until safety level. However, heavy metal accumulation in vegetables cannot be removed by any manners except reducing wastewater use to minimize metal accumulation. The bad odor may come from decomposition of many organic materials discharged to TLR from domestic activities, industry, and hospitals. There is only one way to reduce it is that reducing concentration of organic carbon in wastewaters through treatment and/or supplying less contaminated water from Red river to TLR, which was mentioned previously.

Since To Lich is the last river, receiving all wastewaters from inner Hanoi city before discharging to Nhue River in South Hanoi. To improve quality of TLR, it must be accompanied with improvement of all sewage system including TLR system of four main rivers, 25 other small channels, and 518 lakes of different sizes (Fig. 1.1). Management of small channels and lakes may be difficult, because of illegal disposals of both solid waste and wastewater from citizens to water bodies, and usually environmental regulations do not work well in such situation. In addition, sediment accumulated in lakes or small channels for a long time may contain high level of heavy metals, which has never been dredged, leading to re-suspend to water body if it is not removed completely.

Besides wastewater treatment to improve quality of water bodies in Hanoi city, dredging available sediment, which contains high level of heavy metals, is needed. The point was discussed in Chapter 4 is that the technologies and experiences for treating heavily contaminated sediments are not available, and it is costly, leading to many difficulties for situation in Hanoi. Considering disposal of dredged heavily contaminated sediment to landfill, for a long terms it may become secondary sources of contamination to both surface and underground water. Based on Vietnamese standard, dredged sediment is not suitable for both industrial and agricultural soils, however if we use with small amount for an area of agricultural land it may not affect heavy metal accumulation in both soil and crops, meanwhile crops can use much nutrient and organic carbon available in sediment to reduce input cost and increase income for farmers. However, this point must be scientifically confirmed by further research.

Currently, it costs 0.25 USD/person/months for household solid waste in Hanoi, which is used for management, transportation, and treatment to some extent. The situation for wastewater is not much considered, because no fee is required for transporting and especially wastewater treatment plants are not much available in Hanoi. This should be taken into account as soon as possible by adding cost to volumes of supply water, those cost will be used for wastewater treatment and indirectly may affect behavior of citizens on water use to minimize wastewater discharge.

As discussed in detail in Chapter 2 and Chapter 4, source of heavy metal to TLR is mainly from anthropogenic origin as industry other than domestic activities. The best way to reduce heavy metal contamination in wastewater is to move industrial zones and/or much bearing pollution manufacturers out of inner Hanoi city, which not only affect the environment of water bodies but also on air pollution. Another possibility is management by environmental regulation to force all manufactures to follow solid waste and wastewater, and emission standards, which have been less taken care as result of being rapidly urbanized process. In addition, special taxing on their products for inner city environmental responsibility may be acceptable. Small industry and handicrafts bring many benefits to citizens; however it is difficult in term of environmental protection. The special characteristic of this type of industry in Hanoi city is the scattering distribution, it is not feasible to collect all wastewater for treatment in centralized treatment plant, while treatment at source faces a problem of cost-inefficiency.

5.2. PROJECTION OF METAL LOAD

As mentioned previously, population in TLR basin is growing gradually as a result of natural increase and in-migration; and improved living standard may lead to an increase in water supply demand from 160 liter/person/day in 2005 to 180 in 2010 and to 200 liter/person/day in 2020 (Nguyen 2005). Assuming the metal concentration in 2020 is equivalent to value in 2011, the trend for metal load to Nhue River was projected according to the variation of discharge (Fig 5.1a). The total metal load was also modeled as time progresses (Fig 5.1b). It is the fact that TLR water is not polluted and most under acceptable concentration following Vietnamese standard for irrigation water. However, the total metal load increases year by year as result of elevated wastewater discharge. This amount will be later accumulated in sediment at downstream Nhue River and in a long run it will much affect water quality and environment there. In 2030, total metal load may double in 2011 if no suitable action from government is considered urgently (Fig. 5.1b).

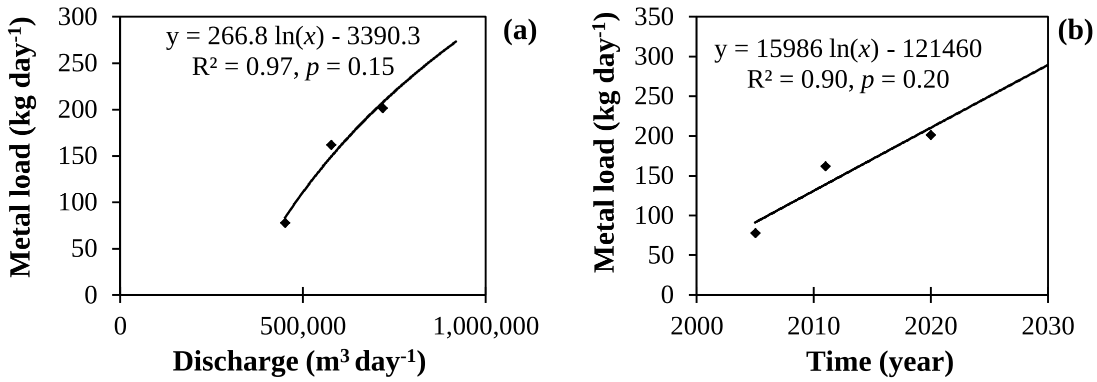

Fig. 5.1. Projected metal load discharged to Nhue River at the end of TLR

5.3. MANAGEMENT IMPLICATIONS

Each country has its own heavy metal standard for irrigation water, agriculture soil, safety environment, etc. In general, developed countries have stricter standards where maximum permissible metal concentrations are much lower than that in developing countries (Fipps 2003). In addition, number of heavy metal included in a standard is also different. Developed countries cover a larger number compared to developing countries (MWI 2001). Biologically, a sole metal highly exceeding permissible concentration may not cause affected, where several metals slightly exceeding permissible concentration may cause heavily affected (Utsumi and Tsuchiya 2002). To integrate number of heavy metals and their permissible concentrations together in a standard, representing possible effects on biota and environment, an integrated standard index (*ISI*) was proposed and calculated as following:

$$ISI = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{SC_i} \qquad (5.1)$$

where C_i is concentration of metal *i* examined in the field, and SC_i is standard/permissible concentration of metal *i*. The values of *ISI* were classified into three classes; *ISI* < 1 (not affected - permissible), 1 ≤ *ISI* < 1.5 (affected - conditionally permissible), and *ISI* ≥ 1.5 (heavily affected - impermissible), which was partly following mean PEC quotients as indicated by MacDonald et al. (2000) and Long et al. (1998) and details were discussed in Chapter 3. The applicability of *ISI* is based on the fact that the appearance of heavy metals in the field is random if they are from natural source and are dependent when they are from anthropogenic sources. In process of releasing heavy metal from anthropogenic sources such as industry, transportation, fertilizing, etc. generally, concentration of heavy metals examined in the field increases or decreases in parallel. Therefore, increasing *ISI* means increasing in concentration of all metals rather than decreasing in concentration of some metals simultaneously with much increasing that of the others. Similarly to national standard, the values of *ISI* classes may also differ country by country. The precise class intervals of *ISI* should be examined by biological experiments on metal accumulation in plants' organs, consequent effects on their consumers, etc.

An example of calculated ISI in TLR indicated that concentration of five concerned metals in sediment much exceeded Vietnamese standard for agricultural soil (Table 5.1). if we consider each metal separately, we may also come to conclusion that sediment from TLR must not be used for agriculture. It may come to the same conclusion from ISI using as the values were greater than 2 in all observed years (Table 5.1).

Table 5.1. Heavy metal concentration (mg/kg) in sediment of various sampling years and integrated standard index (*ISI*)

	Cu	**Zn**	**As**	**Cd**	**Pb**	***ISI***
Sampling in 2011	104.4	547.0	23.1	11.2	76.1	2.69
Sampling in 2005[1]	333.2	390.8	-	9.6	375.3	4.69
Sampling in 1997[2]	158.7	192.7	35.2	-	139.0	2.26
QCVN 03: 2008/BTNMT for agricultural soil[3]	50	200	12	2	70	

[1] cited from Nguyen et al. (2010).
[2] cited from HSDC (1997).
[3] Vietnamese technical regulation on the allowable limits of heavy metals in soils.

Meanwhile, in all seven concerned metals in surface water of TLR (Table 5.2), only Mn concentration observed in years 1997 and 2011 slightly exceeded WHO irrigation water guidelines, strictly based on guidelines we may conclude that wastewater from TLR cannot be used for irrigation. However, using ISI leads to conclusion that it can be used since ISI values are much lower than 1, which may again enlarge usage capability of wastewater for irrigation in the shortage of water resources.

Table 5.2. Heavy metal concentration (μg/L) in water of various sampling years and integrated standard index (*ISI*)

	Cr	**Mn**	**Ni**	**Cu**	**Zn**	**As**	**Pb**	***ISI***
Sampling in 2011	2.6	**220.9**	6.8	4.6	44.4	40.6	7.8	0.23
Sampling in 2005[1]	8.4	114.0	6.0	4.6	31.6	5.6	1.9	0.11
Sampling in 1997[2]	13.0	**220.0**	4.0	20.0	2,000	66.0	160.0	0.43
Irrigation water guidelines[3]	100	**200**	200	200	2,000	100	5,000	

[1] cited from Kikuchi et al. (2009).
[2] cited from HSDC (1997).
[3] WHO (2006).

Except Mn contents in samples of 1997 and 2011, concentrations of other metals in surface water of TLR were still under Vietnamese permissible limit for irrigation water (Table 5.2). As stated in Chapter 1, there are five industrial zones of nearly 100 factories discharging untreated and/or partly treated wastewater to TLR basin. Obviously, many of 100 mentioned factories have been discharging polluted wastewater to TLR system (Nguyen 2005), which is then diluted with other un- or less polluted water sources such as domestic sewage, storm water, agriculture etc. resulting in unpolluted surface water at the end of TLR (Table 5.2). On the other hand, industrial zones or factories may not treat their wastewater; instead they lower concentration by dilution for the purpose of compliance with effluent discharge standard. A stricter standard for heavy metals may be required for study site so called "Total Pollutant Load Control Standard" - TPLCS, which has been applied in developed countries for COD, nitrogen, and phosphorus (JMoE 2011; Moon 2005).

TPLCS (kg/day) has been set as a permissible limit of pollutant discharge load contained in effluents per day for each business establishment in basin and is calculated as Eq. 5.2.

$$TPLCS = C * Q * 10^3 \qquad (5.2), \text{ therefore } C = \frac{TPLCS}{Q * 10^3} \qquad (5.3)$$

where, C is metal concentration in wastewater (mg/L) and Q is wastewater quantity (m^3/day).

General speaking, Q value increases year by year (Table 4.6; 5.3) as result of population growth, freshwater demand increase, and industrial development. Therefore, all business establishments must improve effluent discharge quality/reduce metal concentration in their wastewater through upgrading wastewater treatment facilities and safe operation to comply with TPLCS.

Japanese Ministry of Environment (JMoE 2011) proposed a formula for establishing TPLCS in Japan as following Eq. 5.4.

$$TPLCS = (C_o * Q_o + C_i * Q_i + C_j * Q_j) * 10^3 \qquad (5.4)$$

where, C and Q are concentration and discharge (m^3/day) of the effluent, respectively. C_o*Q_o applied to water volume before July 1, 1980. C_i*Q_i applied to water volume which increased between July 1, 1980 and June 30, 1991. C_j*Q_j applied to water volume which increased after July 1, 1991. Three mentioned period divisions were taken in accordance with the time of construction and expansion of production facilities in Japan.

As a developed country, the quantity of specified effluent is the value declared by factories and business establishments (In Japan, operators must notify officials about the volume and quality of effluent and wastewater treatment method when constructing a new production facility or expanding an existing one). Therefore, the establishment of TPLCS for any areas becomes easy because of availability of previous data on volume and quality of its effluent.

Conversely, in a developing country and being urbanized city like Hanoi, where this study was carried out, many technologies in five industrial zones were established in 1950s and the data on volume and quality of effluent from these industrial zones for the period divisions in accordance with the time of construction and expansion of production were not available. Therefore, a simple formula to estimate TPLCS for TLR in year 2020 (Table 5.3) is proposed as Eq. 5.5.

$$TPLCS_{in\ 2020} = C_{in\ 2020} * Q_{in\ 2020} \qquad (5.5)$$

where, $C_{in\ 2020}$ is the value taken from current standards and guideline for water quality (Table 5.3) and $Q_{in\ 2020}$ is discharge in 2020 as mentioned earlier (Table 4.6). As stated in details, water of TLR has been being used for irrigating agriculture land and since the river runs through dense residential areas with a population of around 2 million people.

Therefore two standards (Vietnamese standard for surface water used for domestic water supply (TCVN 5942-1995, column A) and Vietnamese technical regulation on Water Quality for irrigated agriculture (QCVN 39: 2011/BTNMT) and one guideline (mean concentration of freshwater in the world) were used for three scenarios, which local government may consider achieving water quality of TLR basin in 2020.

Quotient (Table 5.4) was estimated as Eq. 5.6.

$$\text{Quotient (times)} = \frac{\text{Corresponding load}_{\text{in 2020}}}{\text{Surveyed load}_{\text{in 2005 or in 2011}}} \qquad (5.6)$$

Table 5.3. Selected values for heavy metal concentration, corresponding load in 2020, and surveyed load in 2005 and in 2011.

	Cr	Mn	Ni	Cu	Zn	As	Pb
Selected values for metal concentration (µg/L)							
Mean freshwater in the world[1]	1	8	0.5	3	15	0.5	3
TCVN 5942-1995 A, surface water for domestic water supply[2]	100	100	100	100	1000	50	50
QCVN 39: 2011/BTNMT, water quality for irrigation[3]	100	-	-	500	2000	50	50
Corresponding load (kg/day) - TPLCS in 2020							
Mean freshwater in the world	0.72	5.75	0.36	2.16	10.78	0.36	2.16
TCVN 5942-1995 A, surface water for domestic water supply	71.88	71.88	71.88	71.88	718.75	35.94	35.94
QCVN 39: 2011/BTNMT, water quality for irrigation	71.88	-	-	359.38	1437.50	35.94	35.94
Surveyed load (kg/day)							
In 2005	3.79	51.41	2.71	2.07	14.25	2.53	0.86
In 2011	1.15	116.00	4.04	2.31	16.17	16.22	5.77

[1] Median values of freshwater in the world (Bowen 1979).

[2] Vietnamese standard for surface water used for domestic water supply with appropriate treatment.

[3] Vietnamese technical regulation on water quality for irrigated agriculture.

To achieve the first scenario, metal concentrations in water of TLR are under mean concentrations of freshwater in the world, local government must take more actions to reduce metal load in 2020 for example (Table 5.3) 81% for Cr, 95% for Mn, 91% for Ni, and 7%, 33%, 98%, 63% for Cu, Zn, As and Pb, respectively, if we adopt the severer necessary reduction according to the surveyed load in 2005 or 2011. In achieving such figures, not only currently or newly business establishments, but also the oldest technology ones, which were established in 1950s must also improve their production technology and update advanced wastewater treatment technology. This scenario may be infeasible for Hanoi City to achieve in 2020, since it is being urbanized and in stage of limited budget for environmental improvement, compared to others more urgent goals such as promoting economic growth.

In the second scenario, achieving TCVN 5942-1995, column A applied for surface water using for source of domestic with appropriate treatment, the local government must also take actions to reduce metal load of Mn to 38% (Table 5.4) and to maintain the load increase of other metals under acceptable quotients as indicated in Table 5.4. This scenario is more feasible compared to the first one as mentioned previously. To achieve this probably only old business establishments establishing in 1950s with outdated technology are the target for increasing quality of their effluents. Local government may take regular environmental monitoring and inspection to them, supporting them finance in improving technology or in moving out of inner city.

For the last scenario, water quality of TLR must achieve Vietnamese irrigation water standard (QCVN 39: 2011/BTNMT), this is the most feasible scenario in three mentioned. The local government only needs to keep actions, which are being applied to ensure that increase of metal load under acceptable quotients (Table 5.4). For business establishments, they may not need to improve their production technology and change wastewater treatment technology, however they need to control their effluent quantity as current volume. In case, there are any change in effluent quantity they must inform local government for any actions if necessary to ensure the quotient of total load under acceptability.

As stated, the availability of data on quality and quality of effluent of different business establishments in TLR basin are not available. However, toward a friendly environment local government must take actions then such data will be available soon in near future, which may include compositions of effluent of different sources such as industry, domestic sewage, etc. Therefore, practical standard value of metal concentrations will be specifically set according to ratio between household and industrial discharge, type of business establishment in basin of TLR, and the age of applied technologies, which has been widely carried out in developed countries currently.

Table 5.4. Increasing and reducing quotient (times) of metal load in 2020 to that in 2005 and in 2011

	Cr	Mn	Ni	Cu	Zn	As	Pb
Mean freshwater in the world							
2005	-0.81	-0.89	-0.87	1.04	-0.24	-0.86	2.52
2011	-0.38	-0.95	-0.91	-0.07	-0.33	-0.98	-0.63
TCVN 5942-1995 A, surface water for domestic water supply							
2005	18.98	1.40	26.57	34.65	50.44	14.23	41.95
2011	62.24	-0.38	17.78	31.12	44.46	2.21	6.22
QCVN 39: 2011/BTNMT, water quality for irrigation							
2005	18.98			173.26	100.88	14.23	41.95
2011	62.24			155.60	88.91	2.21	6.22

Negative values mean reduction.

The ISI values (Table 5.5) may also indicate the management schemes for local government. Any management scheme is aiming at reducing ISI value to acceptable figure as smaller than 1 as discussed previously. ISI value of the first scenario (mean concentration of freshwater in the world) is 14.8, nearly 15 times of acceptable value. Therefore, much more actions from local government must be carried out. Meanwhile, for the second scenario (TCVN 5942-1995 A for supplying clean water after suitable treatment) fewer actions are required because of lower value of ISI (0.4) as the same discussed in the values of quotient previously. Finally, for the third scenario representing by lowest value of ISI (0.2), no new actions may need to take into account.

Table 5.5. Integrated Standard Index (ISI) of different scenarios

Scenario on water quality achieved in 2020	**Current value of ISI**[1]
Mean freshwater in the world	14.8
TCVN 5942-1995 A for supplying clean water after suitable treatment	0.4
QCVN 39: 2011/BTNMT, irrigation	0.2

[1] ISI was calculated as Eq. 5. 1.

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CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

Heavy metal assessment and source discrimination are important for environmental improvement and protection strategy, especially for urbanizing cities as Hanoi, Vietnam. The concentrations of Mn, Fe, Ni, Cr, Cu, Pb, Zn, As, and Cd were determined to evaluate the level of contamination of To Lich River (TLR) in Hanoi city. All metal concentrations in 0-10 cm water samples, except Mn, were lower than the maximum permitted concentration for irrigation water standard. Meanwhile, concentrations of As, Cd and Zn in 0-30 cm sediments were likely to have adverse effects on agriculture and aquatic life. The sediment was not polluted with Cr, Mn, Fe and Ni, and then pollution level increased in order of Cu < Pb < Zn < As < Cd. As and Mn in sediment were derived from both lithogenic and anthropogenic sources, while Cu, Pb, Zn, Cr, Cd, and Ni originated from anthropogenic sources such as vehicular fumes for Pb and metallic discharge from industrial sources and fertilizer application for other metals. It is concluded that environment of To Lich River has not yet been improved even several regulations on environmental protection had been issued recently.

In nine sampling position along TLR, Cd was the most contaminated metal causing heavy sediment contamination for six sampling positions. Sediments at all sites exceeded maximum permissible concentrations of potentially toxic heavy metal for crops and were considered to be toxic for aquatic life. Cluster analysis demonstrated that the sediment from TLR can be significantly distinguished into three groups in terms of contamination degrees. Accumulation ability of heavy metals in sediment was in order of Cr > Cu > Ni > Zn > Pb > As > Mn based on accumulation coefficient.

To improve quality of TLR, the embankment was carried out in 1998 and finished in 2002. The results indicated that currently there is about 284,000 m^3 sediment accumulated in TLR bed, which is under high contamination of Cr, Mn, Fe, Ni Cu, Zn, As, Cd, and Pb with a total of 7,347 tons of all concerned metals. It may cost up to 170 million USD for treatment. Even though, the technologies and experiences are still limited in study site. Domestic-discharged river reaches received much lower metal loads, roughly 8-28% compared to river reaches of both domestic and industrial inputs. Total load of all nine concerned metals at the end of TLR is 161.7 kg/day, which is finally discharged to Nhue River at South Hanoi. Water quality was improved much right after finishing embankment, then it gradually deteriorated. Meanwhile, sediment quality became even much worse after embankment. Relative river quality index as equal weight for both water and sediment quality indices indicated that quality of TLR was not much improved after the embankment. It even became worse due to the urbanization in recent years. To improve the environmental quality of a river, embankment is not enough and just an initial stage. In the next step, wastewater should be fully treated at sources before discharging to TLR and if possible annual sediment dredging should also be implemented. This not only increases water flow rate, but also reduces re-suspended process of heavy metals from sediment.

Integrated standard index, representing both number of heavy metals and their permissible concentration, should be further considered and encouraged in action for agricultural and environmental standards in the reality of shortage of resource for irrigation water and plants' nutrition. Otherwise, the use of such resources will be banned even concentration of a sole metal slightly exceeds permissible limit.

Three scenarios on Total Pollutant Load Control Standard (TPLCS) for TLR basin were proposed, at which local government may base on to manage the basin toward friendly environment according to their capabilities. The further studies on this topic for establishing practical TPLCS and standard value of metal concentrations for industrial and domestic discharge, business establishments, different types of industry, etc. must be carried out to comply with stricter environmental standard as result of improvement of living standard in near future.

To Lich River is the main river in To Lich River system, which receives untreated wastewater from industry and domestic activities in inner city Hanoi. The deterioration of river quality has caused adverse effects on surrounding environment, and may pose potential threat to human health. In order to improve water quality management, it is necessary to strengthen the monitoring system of water environment with an increase of monitoring points, monitoring frequency and parameters; and a better quality assurance and quality control. In addition, the database should be easily access for publicity, which benefits not only local government but also citizens. These monitoring and information solutions may contribute to a more effective management of quality of To Lich River and all water bodies in Hanoi city in general.